1969

# A Conductance Study of Ion-Solvent Interaction.

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69-17,109

HAMMONDS, Jr., Cecil Noah, 1935-
A CONDUCTANCE STUDY OF ION-SOLVENT INTERACTION.

Louisiana State University and Agricultural and Mechanical College, Ph.D., 1969
Chemistry, inorganic

University Microfilms, Inc., Ann Arbor, Michigan

# A CONDUCTANCE STUDY OF ION-SOLVENT INTERACTION

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by

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January, 1969

ACKNOWLEDGEMENT

The author acknowledges his deep appreciation to Professor M. C. Day, Jr., for his advice, guidance, and encouragement in this research study.

Appreciation is also expressed for the financial assistance provided by the National Science Foundation, which has made the completion of this study possible. This assistance was received in the form of the following grants:

College Teacher Research Participation Program
Louisiana State University, summer sessions
1962, 1963, and 1964

College Teacher Summer Institute Program
Louisiana State University, summer session
1965

Science Faculty Fellowship
Louisiana State University
1966, 1967

Grant for Scientific Research, GP 6421
1968

Finally, the author is grateful for the financial aid provided through the receipt of an award from the Dr. Charles E. Coates Memorial Fund of the L.S.U. Foundation donated by George H. Coates for the preparation of this manuscript.

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## ABSTRACT

Interactions of the sodium ion with tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), triethylamine (TEA), benzene, and toluene in solutions of cyclohexane have been studied by a conductance method at sodium tetra-n-butylaluminate [$NaAl(n\text{-butyl})_4$] concentrations ranging between 0.05 and 0.46 M.

The solubility of $NaAl(n\text{-butyl})_4$ in cyclohexane, a non-interacting solvent, provides a unique and important system for the study of ion-solvent interactions. Since most conventional solvents are basic, a small cation is essential for studies of this type. The addition of controlled amounts of coordinating solvent to a solution containing the sodium ion in a non-coordinating solvent permits the observation of a specific ion-solvent interaction.

Equivalent conductance, viscosity, and density determinations at 25° C are reported for solutions of $NaAl(n\text{-butyl})_4$ at various concentrations in the mixed solvents cyclohexane-THF, cyclohexane-DME, cyclohexane-benzene, and cyclohexane-toluene, and in the pure solvents THF, DME, toluene, and cyclohexane. The equivalent conductance in the mixed systems is reported as a function of the mole ratio base:salt. This conductance data with the results obtained from NMR studies is interpreted in terms of the occurrence of specific ion-solvent interactions. Qualitative interpretation of the viscosity data supports the conclusions observed by means of the conductance studies.

Ion-solvent interactions are not observed between the sodium ion and benzene or toluene. Formation of a strong 1:1 complex with THF and a very weak complex with TEA is observed. A stable 0.5:1 complex with DME is indicated.

The conductance curves of the $NaAl(\underline{n}\text{-butyl})_4$-THF-cyclohexane system for low salt concentrations are interpreted to show the possibility of distinguishing between a specific ion-solvent effect and a solvent dielectric constant effect.

# I. INTRODUCTION

Solvent dielectric constant has generally been considered the most important solvent property affecting the nature of ions in solution. This concept was developed primarily by Fuoss, Kraus, and their students. Their early studies concerned the effect of dielectric constant on the conductance of solutions of tetraisoamylammonium nitrate in dioxane-water mixtures.[1,2] By changing the relative amounts of dioxane and water, they were able to vary the solvent dielectric constant from 2.2 for pure dioxane to 78 for pure water at 25° C. For a constant concentration of salt, they noted a large and continuous decrease in conductance as the dielectric constant of the solvent was lowered. This decrease in conductance was attributed to greater ion association caused by the low dielectric constant of the solvent. As the dielectric constant of the solvent is decreased, new types of interaction products appear. Following the original proposals for ion association by Bjerrum, structures such as ion pairs, triple ions, and neutral ion aggregates of various types were proposed to explain the conductance data for solutions in solvents of low dielectric constant.

Benzene has been one of the most commonly used solvents of low dielectric constant. Conductance data[3] from $10^{-6}$ N to 1 N, cryoscopic data[4] from $10^{-3}$ m to 0.75 m, and molecular polarization values[5] for concentrations above $10^{-5}$ N have been determined for benzene solutions of compounds of the type $R_4N^+X^-$ where R is a large alkyl

group such as isoamyl and X is a picrate, nitrate, or thiocyanate anion. A critical review of this work from dilute solutions to the fused salt is contained in a paper published by Kraus.[6]

While solvents of intermediate and high dielectric constant have been and are widely used in many types of investigations, those of low dielectric constant (<10) have been relatively neglected. The limited solubility of ionic species in non-polar solvents has contributed to this lack of study. However, at the same time, there are advantages to using low dielectric constant solvents. Problems of recent interest in such solvents are: (1) the identification of specific ion-solvent interactions; (2) the establishment of the structure and the properties of the ionic species existing in solution; and (3) the development of theory.

The importance of dielectric constant on ion association and ionic conductance has been recognized since the early work of Fuoss and Kraus. With increasing frequency, however, specific ion-solvent interactions are being cited as significant and possibly more important than the solvent dielectric constant. Until recently, extensive knowledge of the behavior of positive ions in low dielectric media has been limited to the relatively large and probably unsolvated or weakly solvated tetraalkylammonium ions. Experiments concerning specific ion-solvent effects have been primarily studies of solvent interaction with anions. Studies with salts having small cations were not reported until about five years ago. The presence

of a small cation is particularly important in the determination of ion-solvent interactions because of the basic nature of most conventional solvents. In 1958, Kraus summarized what little information that was known of the conductance properties of some cations in various solvents and the interpretation of this experimental data in terms of specific ion-solvent interactions.[7]

While the theory of ion association was approached from a macroscopic viewpoint in terms of the bulk properties of the system by Fuoss, Gilkerson[8] attacked the problem from a microscopic point of view. He developed an equation for the dissociation constant for an ion pair containing three adjustable parameters: (1) the distance of closest approach of the ions; (2) the difference in the solvation energies of the ions and the ion pair; and (3) a function of the free volume available to the ions and the ion pair. The latter two parameters were used to account for specific solvent effects other than that attributed to the solvent dielectric constant.

Cation-ligand association constants have been evaluated from conductance data and interpreted as a measure of ion-solvent interaction.[9] Comparing this technique with others used to investigate ion-solvent interactions, it was concluded that cation-solvent (ligand) interaction in solvents of low dielectric constant depends on the dipole moment and the basic character of the ligand and not on the dielectric constant of the bulk solvent. The interaction of pyridine and tri-n-butylamine with the tri-n-butylammonium cation

and of triphenylphosphine oxide and di-n-butylphosphine oxide with the methyltri-n-butylammonium cation in solutions of o-dichlorobenzene, chlorobenzene, and tetrahydrofuran (THF) were among the systems studied.[10-12]

Although the early studies of ion pairs were primarily by conductance measurements, they have been extensively studied in recent years by spectroscopic and kinetic techniques. The use of kinetic studies gave added significance to the concept of ion pairs when Winstein[13] explained the kinetics of some solvolytic processes by proposing the existence of two types of ion pairs - a contact ion pair and a solvent separated ion pair. These were first observed by Hogen-Esch and Smid in 1966.[14] The existence of solvent separated ion pairs and contact ion pairs and the study of their properties have shown that specific solvent effects other than that due to the solvent dielectric constant do occur. The concepts of ion pairs and ion aggregates is the topic of a review paper by Szwarc.[15] A later publication outlines the limitations and the generalization of the concept of contact and solvent separated ion pairs.[16]

Spectroscopic and conductance measurements demonstrating the formation of both contact and solvent separated ion pairs by alkali metal fluorenyl salts in various solvents of low dielectric constant have been presented by Hogen-Esch and Smid.[14,17] The relative amounts of each type of ion pair depend on the cation size, the temperature and the basicity of the solvent. The fraction of solvent

separated ion pairs formed decreases with increasing ion size from Li to Cs, increases with decreasing temperature, and increases with increasing solvent basicity. Molecules with more than one coordination site are more effective in facilitating the formation of solvent separated ion pairs partly as a result of a smaller entropy loss. In the solvation of these cations, the main factor is the solvating power of the solvent rather than the solvent dielectric constant.

Coordination of solvent molecules with the cation of an ion pair is reflected by NMR spectra. The probable existence of lithium perchlorate and sodium perchlorate as solvated contact ion pairs and of lithium tetraphenylborate and sodium tetraphenylborate as solvent separated ion pairs in THF has been reported.[18] Specific solvation effects by various polyglycol dimethyl ethers on fluorenyllithium solvent separated ion pairs in THF have also been investigated.[19] Nuclear magnetic resonance has been used to detect specific solvation effects in mixed solvent systems containing one strongly solvating component such as diethyl ether or THF and an essentially non-interacting solvent such as hexane or cyclohexane. The solvation of the dimer of butyl lithium by diethyl ether in hexane[20] and of sodium tetra-n-butylaluminate [$NaAl(n\text{-butyl})_4$] by THF in cyclohexane[21] have been studied.

Kinetic studies have been employed to study the degree of aggregation and the type of ionic species present in solution. Anionic polymerizations of the sodium and cesium salts of living

polystyrene in etheral solvents have been used for this type of work. In some instances the reactivity of the solvent separated ion pair may approach that of the free ion.[14,22] The presence of ion aggregates of solvent separated ion pairs was shown by a study of the reactivities in proton abstraction reactions of the fluorenyl salts of Li, Na, and Cs in dioxane, 1,2-dimethoxyethane (DME), and THF.[23] Kinetic measurements have led to the evaluation of an average aggregation number for fluorenyllithium of 5 in DME and THF.

Using the coordinating agent as a probe to reveal the structure of the original ion pair in a given solvent has been proposed.[24] Heats and entropies of coordination derived from conductance measurements on solutions of sodium biphenyl in THF upon the addition of Glyme 3 ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$) and Glyme 4 ($CH_3OCH_2CH_2$-$OCH_2CH_2OCH_2CH_2OCH_3$) gave evidence of isomerism due to different locations of the coordinating agent in the ion pair. The ion pairs of sodium biphenyl coordinated with Glyme 3 are of the contact type indicating the attachment of the ligand to the periphery of the pair. With Glyme 4 a solvent separated ion pair and a solvated contact ion pair are formed.

One of the new techniques applied to the study of ion pairs in solutions of alkali metal salts in solvents of low dielectric constant is electron spin resonance.[25-30] Ion pairs of Li, Na, K, and Cs naphthalenides in solutions of THF and DME are typical of the systems which have been studied. The spectral data was

interpreted in terms of contact and solvent separated ion pairs with the associated equilibria. The interpretation of these results agrees with that given by Hogen-Esch, Smid, Szwarc, and their co-workers for the alkali metal fluorenyl and similar salts in these solvents. The structural and kinetic information which can be obtained from ESR spectra has been summarized by Symons.[31]

In 1964, Day, Barnes, and Cox reported some conductance properties of sodium tetraethylaluminate ($NaAlEt_4$) in toluene and diethyl ether.[32] Since 1962 this research group has engaged in studies of systems containing sodium tetraalkylaluminate salts in low dielectric etheral, saturated hydrocarbon, and mixed solvent systems with the objective of studying ion-solvent interactions. The conductance of compounds of this type in low dielectric constant solvents has been found to be of the same magnitude as that of the tetraalkylammonium salts in dioxane solutions.[1]

Most of the research in this field has been conducted with solvents showing significant ion-dipole interactions. Exceptions have included the studies of the alkali metal picrates and substituted ammonium thiocyanates in benzene.[6,33] An ideal system for studies of ion-solvent interaction is one in which the ions can be considered to be dispersed in a non-solvating medium. The closest approach to such a system is one in which the only ion-solvent interaction is of the ion-induced dipole type. Solutions of sodium tetraalkylaluminates in saturated hydrocarbons fulfill this criterion.

The salts used most extensively by this research group have been $NaAlEt_4$ and $NaAl(\underline{n}\text{-butyl})_4$. Studies with $NaAl(\underline{i}\text{-butyl})_4$ were complicated by the decomposition of the salt at the melting point, which is about 28° C.

The small size of the $Na^+$ ion makes this system unique and important. Since most conventional solvents are basic, a small cation is essential for a study of ion-solvent interactions. Additionally, it is necessary to control the concentration of the coordinating group in order to observe a specific interaction. This requires that the coordinating solvent be added to a solution containing the $Na^+$ ion in a non-coordinating solvent. Conventional salts containing small cations are not soluble to an appreciable extent in these solvents. Thus, the solubility of the sodium tetraalkylaluminates in saturated hydrocarbon solvents creates an especially favorable system for the observation of specific ion-solvent effects.

Conductance measurements of $NaAlEt_4$ in several solvents of low dielectric constant were determined by Trigg.[34] Pyridine, DME, THF, diethyl ether, and cyclohexane-DME mixtures were among the solvents used. He observed a plateau in the conductance curves which he attributed to the formation of a single triple ion of the type +-+ or -+-. The results of these studies as well as the NMR data of Schaschel and Day[21] showed no significant interaction occurs between cyclohexane and the sodium tetraalkylaluminate salt.

The first conductance study in a saturated hydrocarbon solvent was made by Sanders.[35] He attempted to study the effect of

viscosity on conductance by designing an experimental system maintaining the same interaction between the components of the solvent and the electrolyte upon varying the viscosity. The conductance of $NaAl(\underline{n}\text{-butyl})_4$ in cyclohexane-nujol mixtures was determined, while the viscosity was altered by changing the relative amounts of the two solvents. Both of these solvents, being saturated hydrocarbons, were assumed to have nearly the same interaction with the electrolyte because of their similar dielectric constants.

As a result of some studies concerned with specific ion-solvent effects, it seems that in some instances these effects can be more significant than that of the solvent dielectric constant. However, separation of the effects of these two factors on an ionic system has not been possible. Consequently, an independent correlation of these effects with changes in conductance or reaction rates observed in changing from solvent to solvent has not been made. The effect of each of these factors is important because of the large difference in many of the bulk properties of various solvents.

One of the major purposes of this research program is to accomplish a separation of these two effects. The solubility of $NaAl(\underline{n}\text{-butyl})_4$ in cyclohexane, a solvent in which no significant electrolyte-solvent interaction occurs, offers a means of determining the specific effect of ion-solvent interaction with the $Na^+$ ion and an added interacting solvent. From NMR studies the knowledge of the nature of the complex between the $Na^+$ ion and THF permits the

interpretation of the conductance curves at moderate concentrations (0.05177-0.2094 M) of NaAl(n-butyl)$_4$ in cyclohexane solutions with controlled amounts of THF added. Distinguishing between a specific ion-solvent effect and a solvent dielectric constant effect appears possible. Studies of the same system at higher salt concentrations show the possibility of a different conductance mechanism. Finally, the viscosities of the solutions in these systems can be used to interpret qualitatively the behavior of the conducting species.

Studies and interpretation of the conductance and viscosity data for NaAl(n-butyl)$_4$ solutions in cyclohexane with controlled amounts of added DME may suggest possible types of ion aggregates and equilibria which might also occur in the NaAl(n-butyl)$_4$-THF-cyclohexane system. Similarities in the bulk properties of DME and THF (dielectric constant, viscosity, etc.) lead to this expectation with differences between the two systems being ascribed to the greater solvating power of DME, a bidentate coordinating agent. These facts have been demonstrated by some of the studies of the properties of ion aggregates in solutions of these solvents.[36]

The use of triethylamine as a coordinating agent in NaAl(n-butyl)$_4$ solutions in cyclohexane, in contrast to the oxygen containing ethers, shows the formation of a very weak complex with the $Na^+$ ion. This information supports the conclusions reached from previous NMR studies.[21] The conductance results of this system support the major conclusion of the NaAl(n-butyl)$_4$-THF-cyclohexane

studies that a specific ion-solvent effect independent of the solvent dielectric constant is being observed.

Benzene was tested as a potential coordinating agent for the $Na^+$ ion in solutions of NaAl(n-butyl)$_4$ in cyclohexane to determine the extent of interaction between the $\pi$ cloud of the benzene molecule and the $Na^+$ ion. Subsequent information indicating the probable replacement of the alkyl group in the Al(n-butyl)$_4^-$ ion by a phenyl group suggested the use of toluene. The interpretation of the conductance data for the NaAl(n-butyl)$_4$-benzene-cyclohexane and the NaAl(n-butyl)$_4$-toluene-cyclohexane systems is supported by NMR measurements.[37]

A secondary result of these studies indicates the feasibility of a detailed conductance study of cyclohexane solutions of NaAl(n-butyl)$_4$ from very dilute solutions to that of the fused salt.

Current research studies clearly show that with the development of new instruments, methods, and theory, no single technique is powerful enough to give an unambiguous description of the interactions of ionic particles with each other and with the solvent in solvents of low dielectric constant. Conductance, although developed and refined many years ago, is still widely used in addition to more recently developed methods as evidenced by recent reviews of this research area.[38-42] The research reported here has made use of the conductance property as a technique of investigating ion-solvent interactions in low dielectric media; but, the interpretation of the

results depends on data collected by other methods. The results of these studies provide a foundation for future studies and suggest a more complete and extensive investigation of the systems used.

## II. EXPERIMENTAL PROCEDURES

### A. Preparation of NaAl(n-butyl)$_4$

NaAl(n-butyl)$_4$ was prepared by the addition of one mole of Al(n-butyl)$_3$ (198 g) to a sodium dispersion, containing an excess of sodium (ca. 23 g), in 400 ml of n-heptane under a nitrogen atmosphere. The mixture was refluxed for 2 hours. After filtration through a fine fritted glass funnel within a nitrogen dry box, the n-heptane was removed by vacuum evaporation, leaving the salt which was recrystallized from n-pentane at approximately -20° C.

A yield of about 75% was obtained after two recrystallizations from n-pentane. Analysis of pyrophoric materials is quite difficult and rarely satisfactory. The results of the most recent analyses of NaAl(n-butyl)$_4$ are:

| | % Na | % Al | % butyl |
|---|---|---|---|
| Sample 1 | 9.3 | 9.94 | 73.7 |
| Sample 2 | 10.1 | 9.66 | 71.4 |
| Theoretical | 8.3 | 9.71 | 82.0 |

The analysis for aluminum is the only significant one for a test of the purity of the salt. Experimental procedures used for the determination of the % Na and % butyl are not reliable. The direction of the errors in these results is as expected. No report of the preparation of NaAl(n-butyl)$_4$ has appeared in the literature. Thus, data do not exist for comparison with these results. Integration of the NMR spectrum for NaAl(n-butyl)$_4$ dissolved in cyclohexane to

determine the relative number of protons agrees with the proposed formula for NaAl(n-butyl)$_4$.

The melting point of NaAl(n-butyl)$_4$ is 64-66° C. Melting point tubes were filled in the nitrogen dry box, sealed with paraffin wax, and removed in a closed glass vial. A Hoover-Thomas melting point apparatus was used to determine melting points.

B. Solvents

All solvents used were purchased as reagent or higher grade chemicals. Ethers were refluxed for 12 hours over lithium aluminum hydride or calcium hydride. Cyclohexane, toluene, and benzene were refluxed for similar periods over sodium-potassium alloy.

The solvents were distilled under dry nitrogen from a heated 5-foot by 1-inch pyrex column packed with glass helices. A magnetic operated proportional take-off head was set at 80% return to the column. Distillate was removed from the still through a number 18 ball joint. Flasks of various sizes, fitted with two Teflon stopcocks and an inner 24/40 joint with glass cap, were used to collect and store the solvents over sodium chips. Only the middle one-third fraction of the distillate was collected for use. Ethers were used within a period of two to three days after distillation. The other solvents were usually used within similar time periods.

C. Solutions

Standard solutions of $NaAl(\underline{n}\text{-butyl})_4$ were prepared by dissolving the fused salt in the bulk solvent and diluting to volume at room temperature. Aliquot portions of the standard solution were withdrawn by use of a syringe and added to a series of 100 ml volumetric flasks fitted with outer caps to eliminate contamination of the solutions by glass joint lubricant. These flasks were kept sealed until needed for the preparation of the solutions for experimental measurements. Coordinating agents were added by weight to the 100 ml flasks, and the solutions were diluted with the bulk solvent. Final dilution was made at $25^{\circ}$ C in a constant temperature bath by means of a closed dilution apparatus fitted to the flask. A Mettler type P-120 balance within the nitrogen dry box was used for these weighings.

D. Density and Viscosity

Densities of the solvents and the solutions were determined by the use of pycnometers calibrated with distilled water.

Viscosities were obtained by using Cannon-Fenske routine viscometers, size 75, calibrated by the Cannon Instrument Company. Each arm of the viscometer was fitted with 4 mm Teflon stopcocks and number 12 socket joints so that the instrument could be filled in the nitrogen dry box, removed to a constant temperature bath, and connected to a viscometer control apparatus[33] supplied by a dry

nitrogen source. This control apparatus was designed so nitrogen could flow through either arm of the viscometer or be vented to the atmosphere to provide a closed system. This system permits the free flow of the liquid sample in the viscometer under a dry nitrogen atmosphere while equal pressures are maintained on the surface of the liquid in each arm of the instrument. Nitrogen pressure was used to raise the liquid above the meniscus mark of the viscometer. Flow times were measured by an electrically operated timer, manufactured by the Precision Scientific Company, accurate to ±0.1 second. This corresponds to approximately ±0.1% accuracy for the normal flow times obtained. To obtain accurate charges, the viscometers were filled by use of a syringe.

Density and viscosity measurements were determined at 25.00° C, ±0.05° C, in a Sargent Company Model 84810 thermostatically controlled constant temperature bath with thermonitor control. The constant temperature bath was filled with white mineral oil.

E. Conductance

Conductance cells were of the standard design containing shiny platinum electrodes. These cells were fitted with outer glass caps to prevent contamination of the solution by joint lubricant and contained volume capacities from 25 ml to 80 ml. Cell constants were determined by the use of potassium chloride solutions according to the method of Lind, Zwolenik, and Fuoss.[43] These cell constants were between 0.01201 $cm^{-1}$ and 1.441 $cm^{-1}$. Insignificant changes in cell constants occurred over a period of one year.

The pure solvents used were found to have negligible conductances.

Conductance measurements were made by a Leeds and Northrup Model 4666 Jones Modified Conductance Bridge or by a RC-16 Conductance Bridge manufactured by Industrial Instruments, Inc. A Hewlett-Packard Model 200 D audio oscillator and a General Radio Company Type 1232 A tuned amplifier and null detector were used in conjunction with the Leeds and Northrup instrument. The oscillator was operated at 3000 cycles/second and had an output to the bridge of 0.5 volts. Appropriate cells for each solution were selected so that the measured resistances were within the limits of the Jones bridge when possible. The lowest concentration measurable with the Jones bridge is determined by the smallest cell constant available and the 50,000 ohm resistance limit. The upper limit of the RC-16 Conductance Bridge is 2.5 meg ohms.

F. Glassware

Volumetric glassware was thoroughly cleaned with concentrated hydrochloric acid, rinsed with distilled water three times, rinsed with acetone three times, and dried overnight in a 180° C oven. It was then allowed to cool in the evacuated port of the nitrogen dry box. Cells were treated in a similar manner only between successive series of experiments. After rinsing with acetone, they were filled with the bulk non-aqueous solvent being used, allowed

to stand for several hours, dried in air, then dried in the oven overnight. Between measurements for any one series of experiments, the conductance cells and viscometers were cleaned inside the nitrogen dry box with the bulk solvent by rinsing at least three times. These instruments were then filled with this solvent and allowed to stand until use. Before being used, they were emptied and allowed to dry in the nitrogen atmosphere of the dry box.

G. Treatment of Data

Resistance variations were found to follow trends similar to those observed by Trigg.[32] Therefore, the resistance of a given solution was determined at one hour intervals for a period of 6-8 hours after the temperature of the solution had reached 25° C. This was usually assumed to be approximately two hours after placement of the cell in the constant temperature bath. If necessary, Trigg's method of extrapolation back to the time of mixing was used to determine a resistance value. Resistances of pure ether solutions were found to vary more widely than those of solutions containing large quantities of cyclohexane.

Points in each conductance curve were determined randomly. Where possible, different cells were used in a given mole ratio range. This procedure results in the measurement of the properties of the solutions in a given series over a period of 1½-3 days. Where the equivalent conductance, density, and viscosity values of a solution did not follow the trend shown in the series, the data was rejected.

## III. DISCUSSION OF RESULTS

Equivalent conductance, density, and viscosity data at 25° C for several concentrations of $NaAl(\underline{n}\text{-butyl})_4$ in cyclohexane containing varying amounts of THF, DME, benzene, toluene, and triethylamine are given in Tables 2, 4, 6, 7, and 8. Tables 1, 3, and 5 contain similar data for solutions of $NaAl(\underline{n}\text{-butyl})_4$ in the pure solvents cyclohexane, THF, and DME. Some physical properties of the solvents and of the added coordinating agents are presented in Table 9. Figures 1-10 present the data contained in Tables 1, 2, 4, 6, 7, and 8.

### A. Conductance of Cyclohexane Solutions of $NaAl(\underline{n}\text{-butyl})_4$ and $NaAlEt_4$

Comparing the conductance properties of $NaAl(\underline{n}\text{-butyl})_4$ with those of $NaAlEt_4$ determined by Trigg[34] in the same solvents gives support to the general assumption that complexation occurs only through the cation in these systems. The equivalent conductances of solutions of $NaAlEt_4$ and $NaAl(\underline{n}\text{-butyl})_4$ in THF are respectively 16.98 $cm^2$ $ohm^{-1}$ $eq^{-1}$ at a concentration of 0.02703 M and 19.02 $cm^2$ $ohm^{-1}$ $eq^{-1}$ at a concentration of 0.05316 M. For DME solutions of these salts, the equivalent conductance range is 18.01-21.58 $cm^2$ $ohm^{-1}$ $eq^{-1}$ for $NaAlEt_4$ solutions at concentrations of 0.06253-0.1466 M and 18.17-23.99 $cm^2$ $ohm^{-1}$ $eq^{-1}$ for $NaAl(\underline{n}\text{-butyl})_4$ solutions at concentrations of 0.05177-0.2017 M. While the data presented is sparse, it tends to demonstrate that conductance in similar solutions of

$NaAlEt_4$ and $NaAl(\underline{n}\text{-butyl})_4$ is due to the same species of complexed $Na^+$ ion.

B. Degree of Aggregation

Interpretation of the conductance data presented in Figures 1-10 depends to some extent on the state of aggregation of $NaAl(\underline{n}\text{-butyl})_4$ in cyclohexane. Attempts to determine the degree of aggregation of this salt in cyclohexane by vapor pressure osmometry and freezing point depression measurements have been inconclusive. Preliminary indications show that $NaAl(\underline{n}\text{-butyl})_4$ may exist as a dimer or trimer in the concentration range used in these studies.[44]

Solutions of salts in solvents of low dielectric constant are generally considered to be only slightly dissociated into free ions even at the lowest concentrations at which reliable measurements can be made. Fuoss and Kraus propose that an equilibrium exists between free ions and ion pairs of tetraalkylammonium salts dissolved in benzene at concentrations below the conductance minimum which occurs at concentrations of the order of $10^{-5}$ M for these solutions. At higher concentrations they propose that higher aggregates occur.[45]

Few studies in solvents of low dielectric constant have been made in which the cation is small. Trigg[34] studied the conductance of $NaAlEt_4$ in several solvents. He explained the plateau in the conductance curves of $NaAlEt_4$ in pyridine, THF, DME, and mixtures of DME-cyclohexane at concentrations of 0.002-0.022 M as due to the formation of only one type of triple ion.

More recently studies of ion pairs containing the $Na^+$ ion have been made in low dielectric constant solvents by spectral, kinetic, conductance and ESR techniques.[14,23,28-30] Generally these have been made at sufficiently low concentrations that triple ions or higher aggregates are not expected to exist. For this reason they are of little value in interpreting our data.

Attempts by our research group to extend conductance measurements of $NaAl(\underline{n}\text{-butyl})_4$ solutions in cyclohexane to concentrations less than 0.05 M have been unsuccessful. However, combination of the data presented in this research study for 0:0 mole ratios of coordinating agent to $NaAl(\underline{n}\text{-butyl})_4$ in cyclohexane with a study by Ahmad[46] for the 0.11-1.13 M concentration range indicate it may be possible to obtain meaningful values at lower concentrations. This data is presented in Table 1 and Figure 1.

At concentrations above 0.1 M the conductance curve of solutions of $NaAl(\underline{n}\text{-butyl})_4$ in cyclohexane is essentially flat. This level portion may indicate the presence of similar conducting species as well as an increasing degree of ion aggregation. Below this concentration the conductance increase may be due to a dissociation of the ion aggregates into less complex conducting species. In the concentration range studied, an equilibrium may exist between some type of ion aggregate and some dissociated ionic species.

Figure 1 shows a possible trend and the need for additional study of this system. Because of the high resistances of the

TABLE 1

EQUIVALENT CONDUCTANCES, DENSITIES, AND VISCOSITIES OF

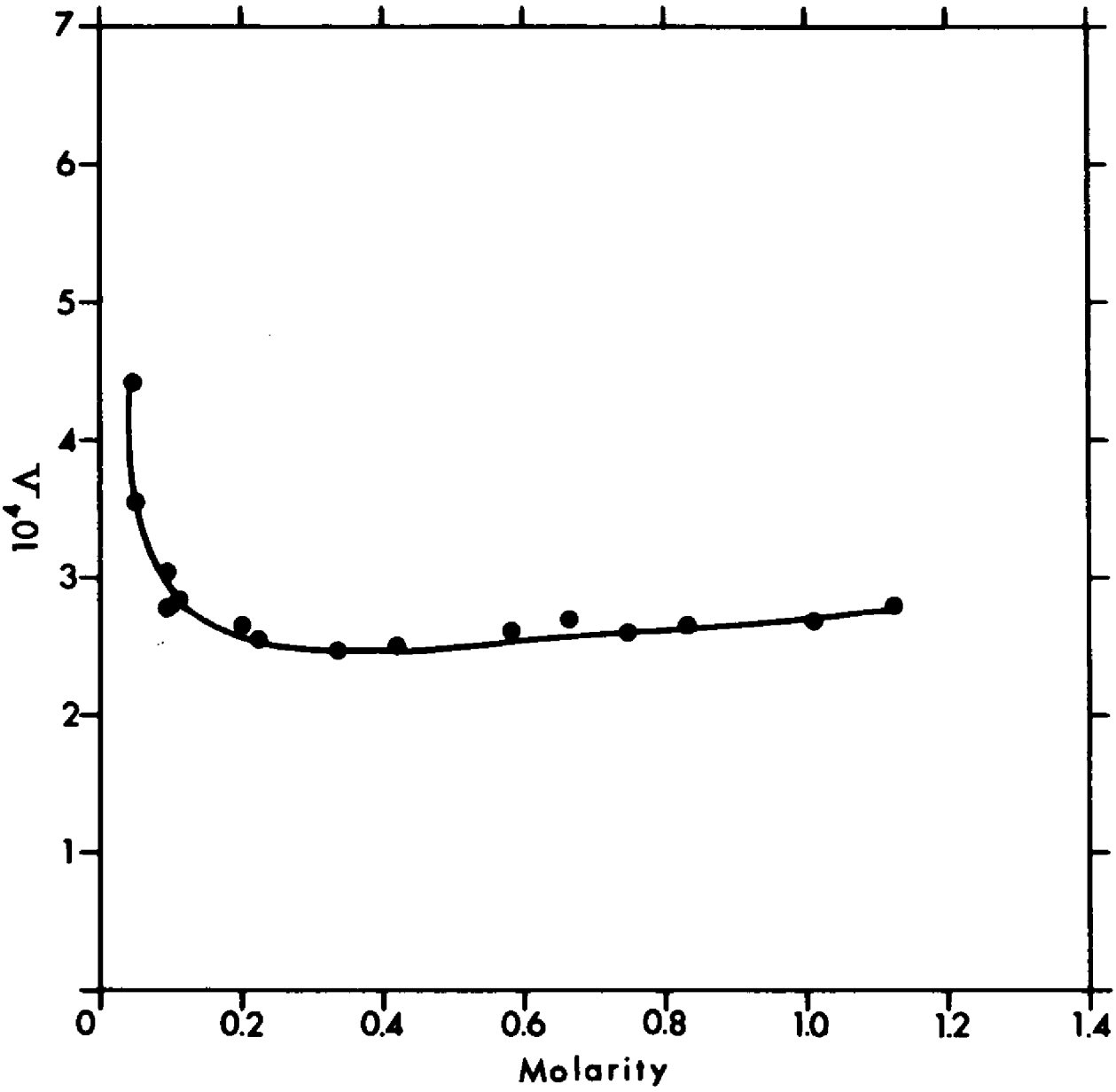
$NaAlBu_4$-CYCLOHEXANE SOLUTIONS

| Molarity eq $l^{-1}$ | $10^4 \Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| 0.04776 | 4.146 | 0.7740 | 13.8 |
| 0.05213 | 3.544 | 0.7747 | 15.5 |
| 0.09524 | 2.769 | 0.7752 | 14.9 |
| 0.1032 | 2.798 | 0.7759 | 23.8 |
| 0.1125* | 2.837 | 0.7807 | 24.8 |
| 0.2023 | 2.654 | 0.7786 | 26.2 |
| 0.2249* | 2.551 | 0.7830 | 32.1 |
| 0.3374* | 2.480 | 0.7855 | 53.1 |
| 0.4218* | 2.508 | 0.7896 | 67.3 |
| 0.4683 | 3.127 | 0.7855 | 70.0 |
| 0.5825* | 2.614 | 0.7956 | 91.6 |
| 0.6657* | 2.696 | 0.7922 | 105 |
| 0.7489* | 2.606 | 0.7962 | 122 |
| 0.8321* | 2.654 | 0.7982 | 154 |
| 1.012* | 2.683 | 0.8052 | 186 |
| 1.125* | 2.793 | 0.8060 | 222 |

*N. Ahmad[46]

FIGURE 1

EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE



solutions, the data obtained in this work require the use of the RC-16 conductance bridge and cells with low cell constants. A concentration-conductance study and one determining the degree of aggregation of NaAl(n-butyl)$_4$ in cyclohexane extending to low concentrations would allow determination of the ionic species in solution as well as the association constants for ion aggregates. From temperature dependent conductance studies, heats of dissociation could be found. Cryoscopic techniques could be used to determine the type of particles present in these solutions. These studies would provide a test for the theories developed by Fuoss and Kraus to explain the behavior of electrolytes in low dielectric constant solvents. Since their studies were made with salts containing the large tetraalkylammonium cation, the use of the relatively small $Na^+$ ion provides a uniquely different system. The equivalent conductance of NaAl(n-butyl)$_4$ in cyclohexane is of the order of a magnitude of 10 greater than that of the tetraalkylammonium salts in dioxane solutions at similar concentrations, thus demonstrating the ionic nature of this salt.[1]

## C. Ion-solvent Interaction: $Na^+$-THF

Figure 2 shows the equivalent conductance of 0.05213 M, 0.09524 M, and 0.1525 M NaAl(n-butyl)$_4$ solutions as a function of the mole ratio of THF to salt using cyclohexane as a solvent. Figures 3 and 4 show similar studies made at NaAl(n-butyl)$_4$ concentrations of 0.2094 M, and 0.2654 M and 0.4683 M. A complete study

study of the system from pure cyclohexane to pure THF for 0.2094 M NaAl(n-butyl)$_4$ solutions is presented in Figure 5. Corresponding equivalent conductance, density, and viscosity data are given in Table 2.

1. Conductance

The general form of the conductance curves for the NaAl-(n-butyl)$_4$-THF-cyclohexane system at mole ratios less than 8:1 is similar. At approximately a ratio of 1:1 a peak occurs, followed by a drop, a subsequent plateau, and a sharp rise. With increasing salt concentration the peak and plateau regions vary as well as showing greater equivalent conductances. The plateau region appears to approach the value of the equivalent conductance of the 1:1 complex, but vanishes at high concentrations of NaAl(n-butyl)$_4$. The inflection points observed at the THF:NaAl(n-butyl)$_4$ mole ratios of 1:1 and 4:1 tend to disappear at salt concentrations above 0.2654 M. The concentration at which this change occurs was not determined.

Solutions of 0.4683 M NaAl(n-butyl)$_4$ in cyclohexane contain approximately 25% by volume of NaAl(n-butyl)$_4$ at 64° C, the temperature of fusion of this salt. Thus, the solution is highly concentrated and the conductance curve may indicate a conductance mechanism different from that in the less concentrated solutions. A Grotthaus type mechanism involving the transfer of an ion from one aggregate to another might explain the conductance properties of this system.

TABLE 2

EFFECT OF THF ON THE EQUIVALENT CONDUCTANCES,

DENSITIES, AND VISCOSITIES OF $NaAlBu_4$-CYCLOHEXANE SOLUTIONS

| Ratio THF:$NaAlBu_4$ | $10^3 \Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| ----------0.05213 M $NaAlBu_4$---------- | | | |
| 0.00 | 0.3544 | 0.7747 | 15.5 |
| 0.25 | 3.550 | 0.7748 | 11.9 |
| 0.51 | 4.378 | 0.7748 | 10.5 |
| 0.77 | 7.127 | 0.7754 | 9.78 |
| 1.02 | 7.624 | 0.7745 | 9.66 |
| 1.27 | 5.325 | | |
| 1.51 | 3.413 | 0.7742 | 9.95 |
| 1.81 | 0.9975 | 0.7756 | 9.39 |
| 2.05 | 0.6678 | 0.7762 | |
| 2.29 | 0.5691 | 0.7760 | 9.39 |
| 2.53 | 0.5360 | 0.7770 | 9.42 |
| 2.79 | 0.5287 | | |
| 3.04 | 0.5357 | | |
| 3.39 | 0.3375 | 0.7765 | 9.31 |
| 3.58 | 0.4970 | | |
| 3.79 | 0.5767 | 0.7758 | 9.39 |
| 4.05 | 0.5837 | 0.7776 | 9.46 |
| 4.28 | 0.5903 | 0.7768 | 9.36 |
| 4.87 | 0.7498 | 0.7771 | 9.35 |
| 4.96 | 0.8193 | 0.7774 | 9.29 |
| 5.55 | 1.151 | 0.7785 | 9.31 |
| 6.09 | 1.032 | | |
| 7.14 | 1.176 | 0.7784 | 9.26 |
| ----------0.09524 M $NaAlBu_4$---------- | | | |
| 0.00 | 0.2769 | 0.7752 | 14.9 |
| 0.31 | 3.126 | 0.7763 | 14.5 |
| 0.73 | 12.69 | 0.7767 | 10.8 |
| 1.13 | 22.22 | 0.7775 | 10.6 |
| 1.32 | 22.60 | 0.7776 | 10.3 |
| 1.56 | 19.05 | 0.7778 | 10.1 |
| 1.82 | 15.38 | 0.7781 | 10.1 |
| 2.07 | 7.250 | 0.7764 | 9.82 |
| 2.29 | 4.675 | 0.7787 | 9.84 |
| 2.39 | 4.415 | 0.7783 | 9.81 |
| 2.66 | 4.278 | 0.7792 | |
| 3.10 | 3.927 | | |
| 3.49 | 4.165 | 0.7797 | 9.75 |

| Ratio THF:$NaAlBu_4$ | $10^3$ Λ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| | 0.09524 M $NaAlBu_4$ (Cont.) | | |
| 3.98 | 5.586 | 0.7805 | 9.81 |
| 4.15 | 5.470 | 0.7806 | |
| 4.36 | 7.437 | | |
| 4.81 | 8.526 | 0.7810 | 9.84 |
| 5.29 | 9.214 | 0.7819 | 9.63 |
| 6.36 | 16.23 | 0.7821 | |
| 7.33 | 25.14 | 0.7829 | 9.62 |
| | 0.1525 M $NaAlBu_4$ | | |
| 0.28 | 4.218 | 0.7779 | 22.3 |
| 0.49 | 9.960 | 0.7784 | 17.0 |
| 0.76 | 25.87 | 0.7783 | 14.3 |
| 1.00 | 66.12 | 0.7782 | 11.5 |
| 1.25 | 60.22 | 0.7793 | 11.5 |
| 1.76 | 56.50 | 0.7806 | 10.6 |
| 1.99 | 32.67 | 0.7813 | 10.4 |
| 2.31 | 32.23 | 0.7818 | |
| 2.52 | 31.34 | 0.7832 | |
| 2.78 | 26.36 | 0.7827 | 10.7 |
| 2.99 | 31.68 | 0.7820 | 10.4 |
| 3.25 | 31.90 | 0.7836 | 10.4 |
| 3.49 | 33.32 | 0.7837 | 10.4 |
| 3.75 | 39.57 | 0.7841 | 10.4 |
| 4.02 | 68.11 | | |
| 4.27 | 54.54 | 0.7862 | 10.5 |
| 4.51 | 49.64 | 0.7860 | 10.5 |
| 5.02 | 101.8 | 0.7853 | 10.7 |
| 5.44 | 107.4 | 0.7864 | 10.3 |
| 5.49 | 136.5 | 0.7856 | 10.1 |
| 6.54 | 180.2 | 0.7843 | 10.3 |
| 7.30 | 253.1 | 0.7879 | 10.3 |

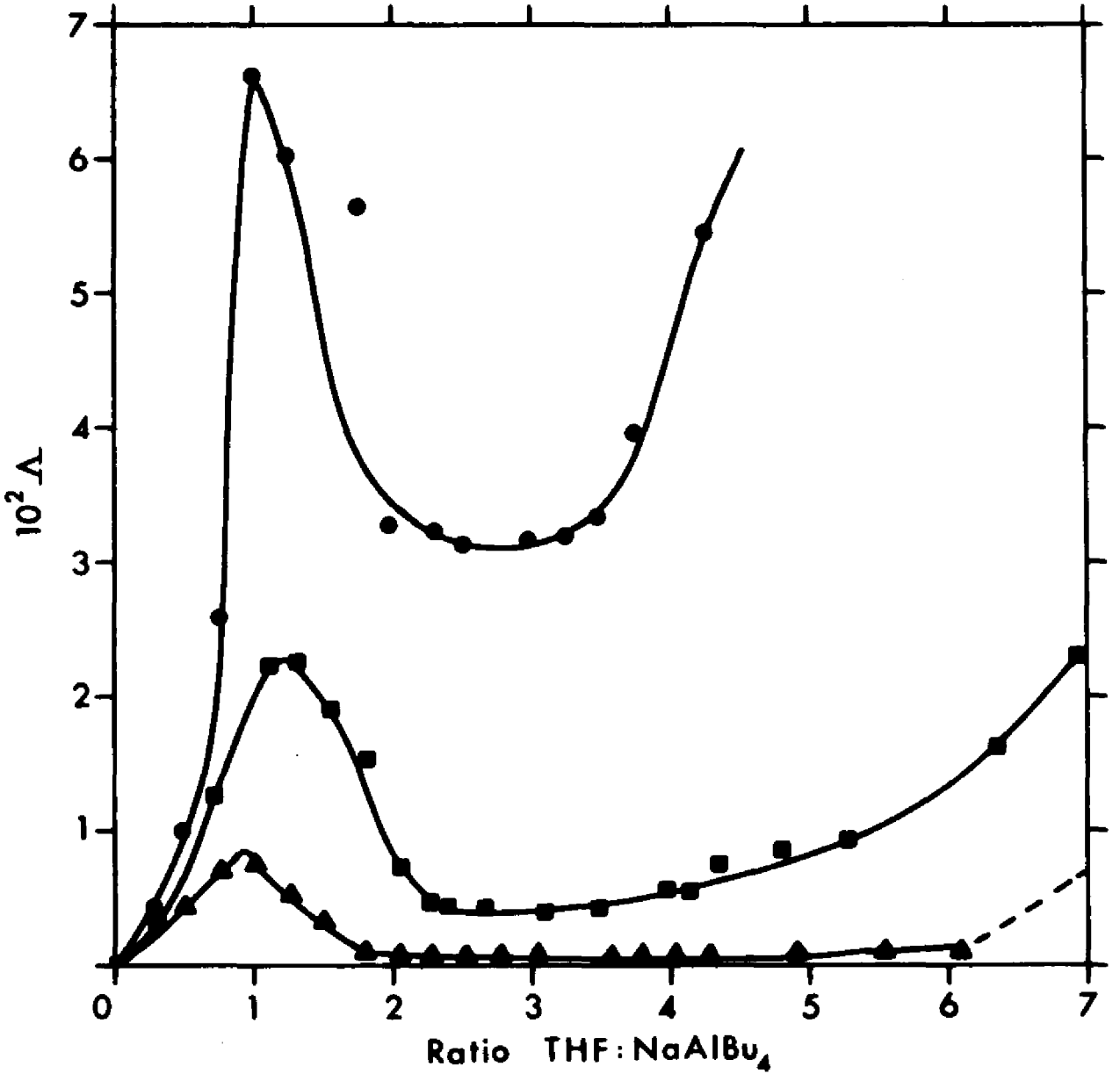
| Ratio THF:$NaAlBu_4$ | 10 $\Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| ----------0.2094 M $NaAlBu_4$---------- | | | |
| 0.00 | 0.002911 | 0.7998 | 36.9 |
| 0.23 | 0.02767 | 0.7806 | 33.6 |
| 0.49 | 0.1147 | 0.7792 | 22.7 |
| 0.74 | 0.2756 | 0.7814 | 17.7 |
| 1.00 | 0.6788 | 0.7813 | 14.4 |
| 1.22 | 1.000 | 0.7820 | |
| 1.51 | 1.527 | 0.7840 | 13.2 |
| 1.75 | 1.816 | 0.7869 | 12.2 |
| 1.97 | 1.319 | 0.7841 | 11.4 |
| 2.22 | 1.215 | | |
| 2.49 | 0.9239 | 0.7855 | 11.2 |
| 2.89 | 1.464 | 0.7888 | 11.2 |
| 2.99 | 1.255 | 0.7883 | 11.6 |
| 3.24 | 1.279 | 0.7889 | 11.7 |
| 3.52 | 1.600 | 0.7896 | 11.7 |
| 3.74 | 1.686 | 0.7898 | 11.5 |
| 4.01 | 2.131 | 0.7897 | 11.7 |
| 4.33 | 2.763 | 0.7903 | 11.9 |
| 4.69 | 3.630 | 0.7915 | 11.8 |
| 5.01 | 4.055 | 0.7910 | 11.7 |
| 5.57 | 4.878 | 0.7895 | 11.6 |
| 6.03 | 6.100 | 0.7927 | 11.9 |
| 6.59 | 5.807 | 0.7937 | 11.4 |
| 7.01 | 8.017 | 0.7946 | 11.1 |
| 8.03 | 9.657 | 0.7966 | 12.0 |
| 8.77 | 15.36 | 0.7926 | 11.9 |
| 10.00 | Two Phases | | |
| 14.14 | Two Phases | | |
| 18.01 | 35.10 | 0.8160 | 11.1 |
| 20.08 | 43.97 | 0.8197 | 10.4 |
| 21.98 | 48.49 | 0.8230 | 9.93 |
| 27.28 | 72.63 | 0.8338 | 9.06 |
| 30.28 | 85.91 | 0.8391 | 8.67 |
| 34.07 | 106.4 | 0.8468 | 8.29 |
| 36.43 | | 0.8499 | 7.98 |
| 39.01 | 133.7 | 0.8565 | 7.78 |
| 43.94 | 161.3 | 0.8663 | 7.41 |
| 45.75 | 155.9 | 0.8694 | 7.25 |
| 47.05 | | 0.8719 | 7.17 |
| 49.06 | 187.7 | 0.8734 | 7.09 |
| 51.19 | | 0.8802 | 6.90 |
| 52.44 | 206.6 | 0.8835 | 6.82 |
| 53.28 | 198.9 | 0.8849 | 6.87 |
| 54.97* | 202.6 | 0.8877 | 6.70 |

*Pure THF Solution

| Ratio THF:$NaAlBu_4$ | 10 $\Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| | 0.2654 M $NaAlBu_4$ | | |
| 0.32 | 0.05904 | | |
| 0.92 | 0.5871 | | |
| 1.15 | 0.9620 | | |
| 1.47 | 1.163 | | |
| 2.18 | 0.9376 | | |
| 3.04 | 1.745 | | |
| 3.46 | 2.559 | | |
| 4.00 | 3.689 | | |
| 4.59 | 4.991 | | |
| 4.96 | 5.863 | | |
| 5.96 | 7.769 | | |
| 7.04 | 10.22 | | |
| 8.23 | 13.68 | | |
| 8.26 | 12.03 | | |
| 10.86 | 18.54 | | |
| | 0.2880 M $NaAlBu_4$ | | |
| 0.00 | 0.004945 | 0.7826 | 43.9 |
| 0.30 | 0.04280 | | |
| 0.47 | 0.09704 | 0.7832 | 18.3 |
| 0.88 | 0.3949 | 0.7847 | 16.9 |
| 1.15 | 0.6739 | | |
| 1.17 | 0.8041 | 0.7861 | 13.9 |
| 2.13 | 0.9771 | | |
| 2.52 | 1.377 | | |
| 3.29 | 1.853 | 0.8153 | 13.6 |
| 3.60 | 2.258 | | |
| 3.93 | 3.217 | 0.8049 | 13.9 |
| 4.71 | 5.513 | 0.8055 | |
| 9.00 | 17.57 | 0.8184 | 13.8 |
| | 0.4683 M $NaAlBu_4$ | | |
| 0.00 | 0.003127 | 0.7910 | 70.0 |
| 0.30 | 0.05897 | 0.7910 | 44.4 |
| 0.71 | 0.4047 | 0.7956 | 32.5 |
| 0.74 | 0.4511 | 0.7892 | 31.2 |
| 1.04 | 1.244 | 0.7897 | 21.2 |
| 1.38 | 2.359 | 0.7880 | 18.1 |
| 1.80 | 3.575 | 0.7905 | 16.8 |
| 2.31 | 3.867 | 0.7940 | 15.9 |
| 2.95 | 4.394 | 0.8117 | 16.5 |
| 3.41 | 6.174 | 0.8060 | 16.8 |
| 3.79 | 9.151 | 0.8072 | 17.0 |
| 4.12 | 11.38 | 0.8083 | 17.1 |
| 4.76 | 19.10 | 0.8147 | 17.7 |
| 7.63 | 37.09 | 0.8374 | 17.4 |

FIGURE 2

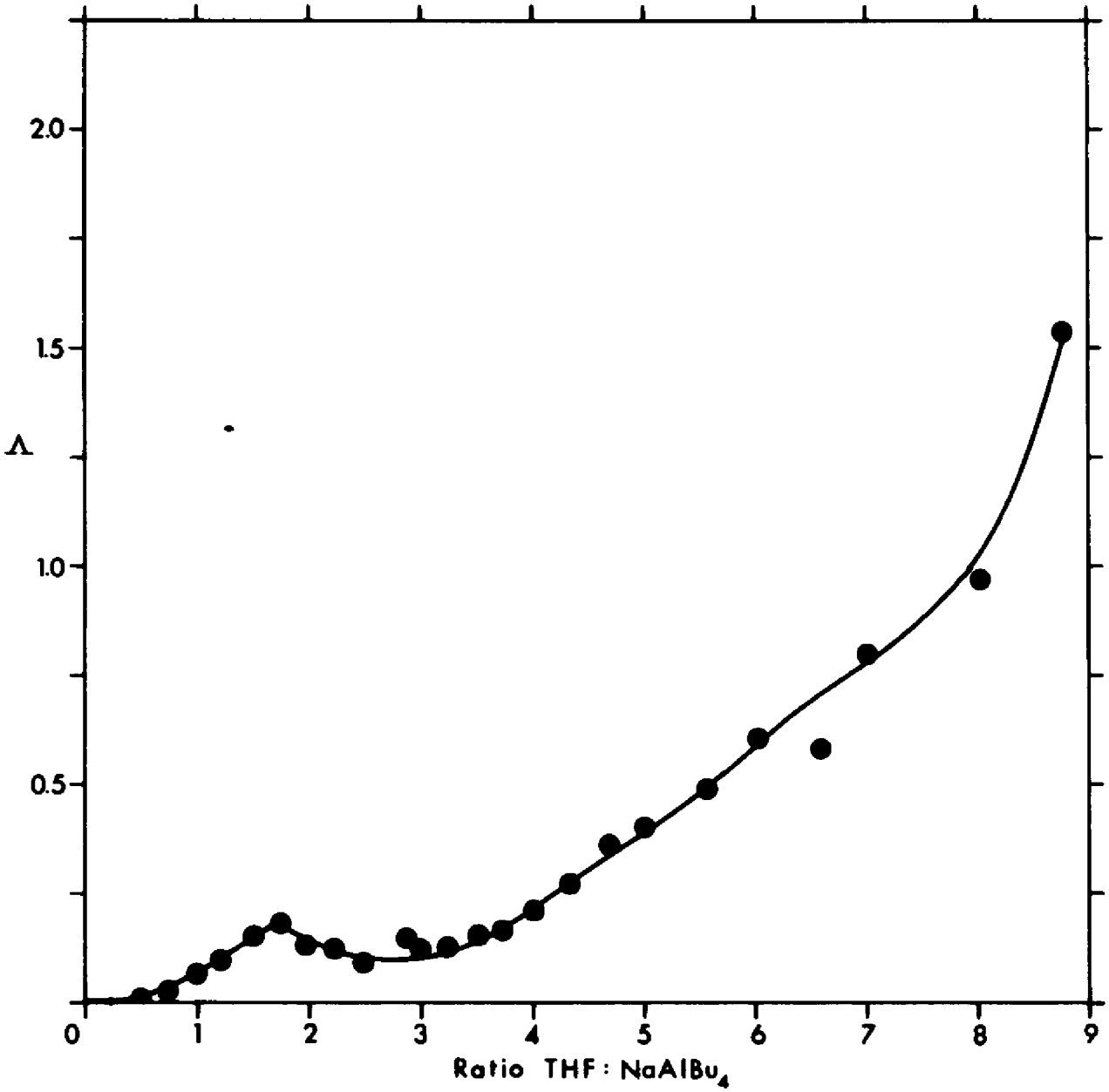
EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE–THF MIXTURES AS A FUNCTION OF THE MOLE RATIO THF:$NaAlBu_4$




Concentration $NaAlBu_4$: ▲ – 0.05213 M, ■ – 0.09524 M, ● – 0.1525 M

FIGURE 3

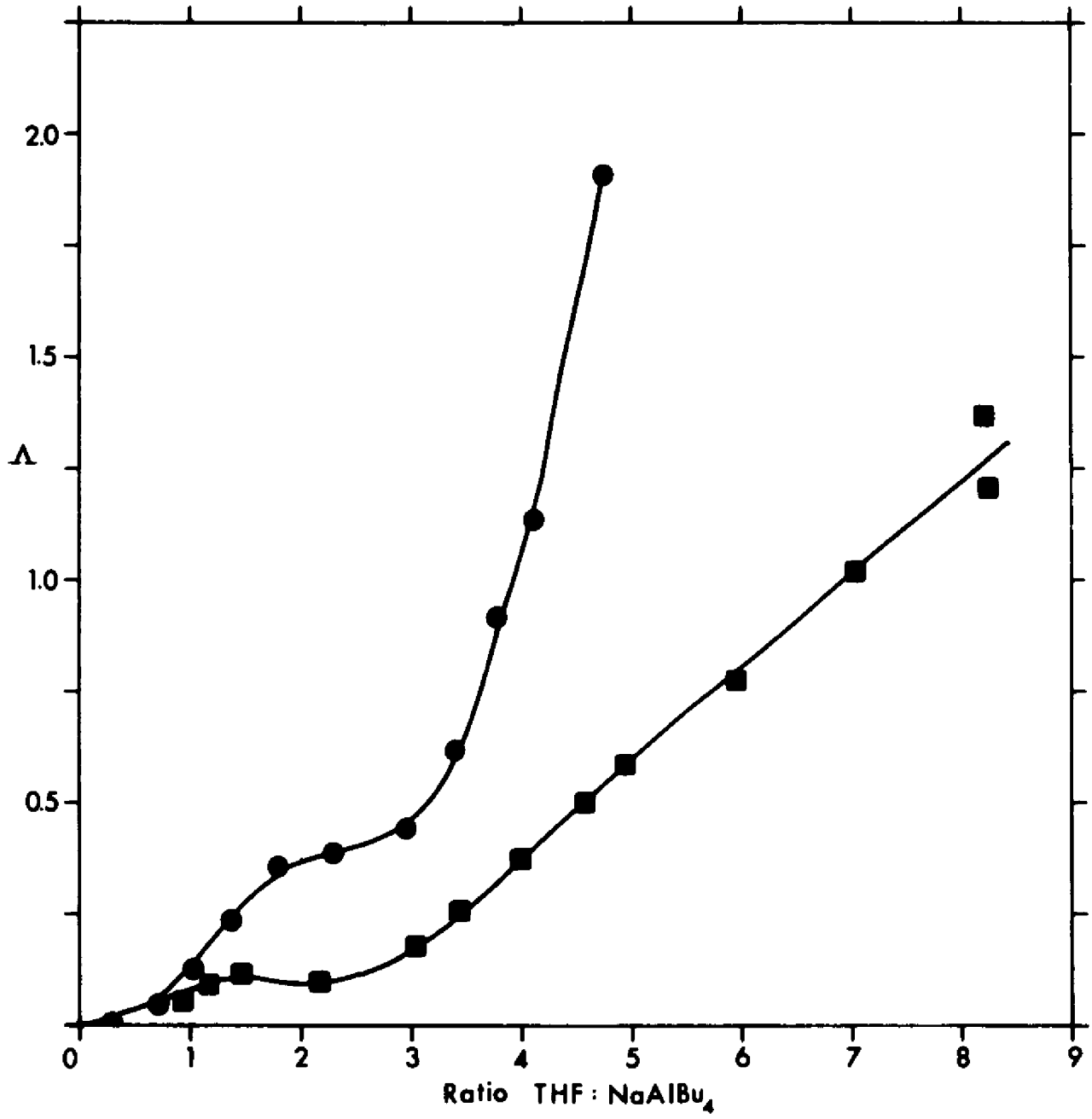
EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE–THF MIXTURES AS A FUNCTION OF THE MOLE RATIO THF:$NaAlBu_4$




Concentration $NaAlBu_4$ = 0.2094 M

FIGURE 4

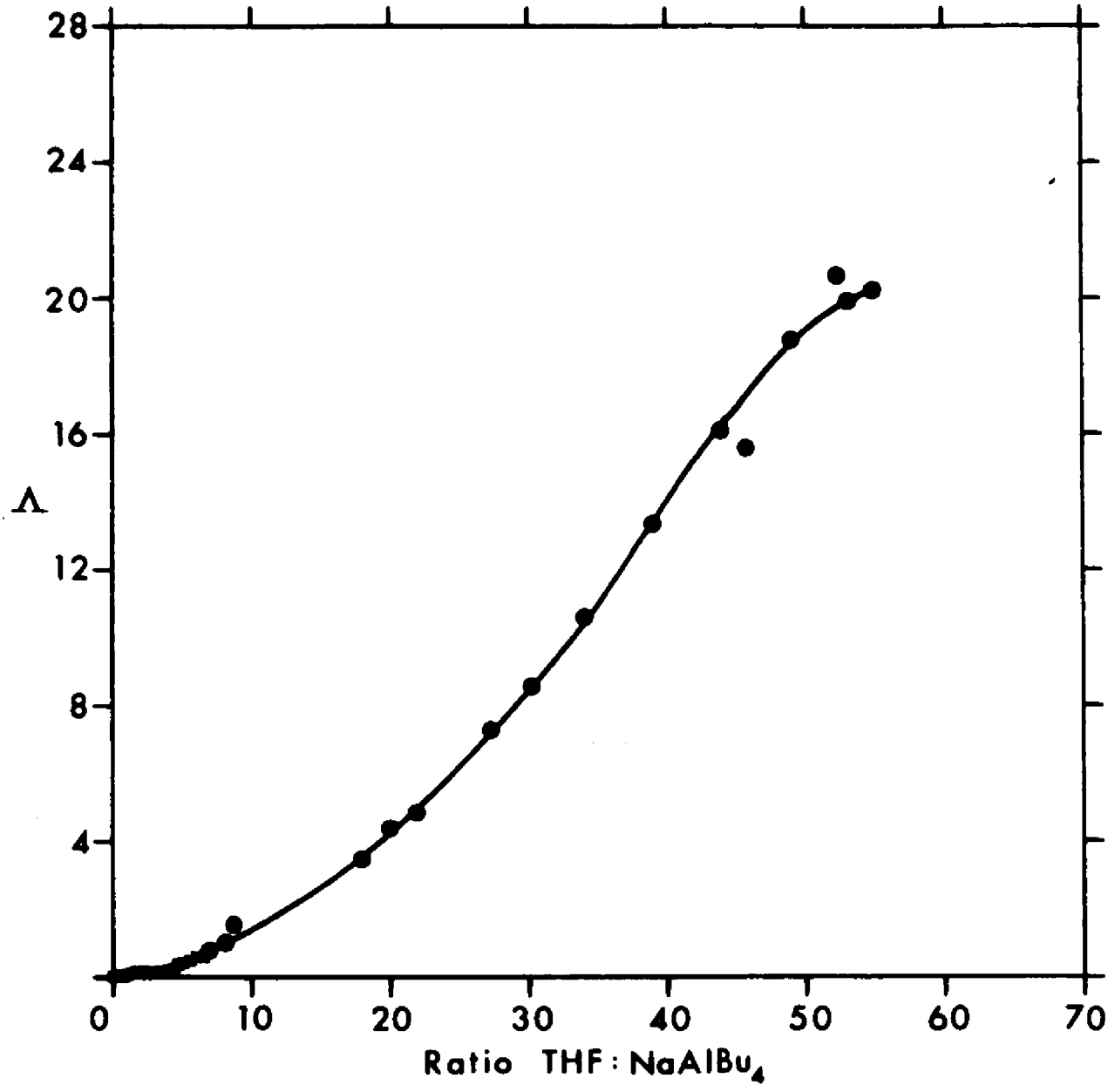
EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE–THF MIXTURES AS A FUNCTION OF THE MOLE RATIO THF:$NaAlBu_4$




Concentration $NaAlBu_4$: ■ – 0.2654 M, ● – 0.4683 M

FIGURE 5

EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE–THF MIXTURES FROM PURE CYCLOHEXANE TO PURE THF AS A FUNCTION OF THE MOLE RATIO $THF:NaAlBu_4$




Concentration $NaAlBu_4$ = 0.2094 M

Nuclear magnetic resonance studies of the complexation of the $Na^+$ ion by THF using cyclohexane as a solvent have shown that a stable 1:1 complex exists with three additional molecules of THF in equilibrium with this complex.[21] Since no significant interaction occurs between $NaAl(\underline{n}\text{-butyl})_4$ and the solvent, cyclohexane, the solvent can be considered as a dispersing medium for the salt. This knowledge of the nature of the THF complex with the $Na^+$ ion can be used to interpret the conductance curves of this system.

Ion aggregates containing solvent separated ion pairs have been shown to exist. This has been done for both fluorenyllithium and fluorenylsodium in THF.[23] Thus, THF might complex with the $Na^+$ ion in the ion aggregate. This increase in effective cation size will decrease the stability of the ion aggregate. Furthermore, it is reasonable to conclude from measurements of the conductance of cyclohexane solutions of $NaAl(\underline{n}\text{-butyl})_4$ that the principal charge carrier present is the $Na^+$ ion. Complexation of the $Na^+$ ion, resulting from an equilibrium between an undissociated neutral ion aggregate and its ions, could cause a shift in the position of equilibrium toward that of the undissociated species. Therefore, the stable 1:1 $Na^+$ ion THF complex can be formed by either of these two possible paths.

The stability of the 1:1 complex explains the steep rise in conductance from 0:0 to 1:1 mole ratios of $THF:NaAl(\underline{n}\text{-butyl})_4$. All free $Na^+$ ion is essentially complexed at the 1:1 ratio and the

predominate equilibrium may be:

$$NaTHF^{+}Al(\underline{n}\text{-butyl})_4^{-} = NaTHF^{+} + Al(\underline{n}\text{-butyl})_4^{-}$$

After the formation of the 1:1 complex the decrease in the equivalent conductance can be attributed to a decrease in the mobility of the $Na^{+}$ ion as a result of additional complexation. A rapid rise in conductance beginning at or just prior to the 4:1 ratio in all cases rises to nearly the same value as shown by the data in Table 3. An equilibrium in which a relatively stable 4:1 complex is formed is indicated:

$$NaTHF^{+} + 3\ THF = Na{\cdot}4THF^{+}$$

The rise in the equivalent conductance after the 4:1 ratio would be expected because of the increase in solvent dielectric constant corresponding to the increasing amount of free THF in the bulk solvent. Figure 5 shows an increase of about 300 relative to the maximum equivalent conductance at the 1:1 ratio.

Between 10:1 and 15:1 ratios two immiscible phases form. At higher mole ratios homogeneous solutions are formed and conductance properties can again be determined. A continuous rise in equivalent conductance occurs due to a continuous increase in the dielectric constant of the solvent system and the decreasing viscosity of the solution upon the addition of larger amounts of THF.

2. Viscosity

The viscosity of a salt solution is a measure of the shearing force required to move one layer of solution with respect to

TABLE 3

EFFECT OF CONCENTRATION ON THE EQUIVALENT CONDUCTANCES, DENSITIES, AND VISCOSITIES OF $NaAlBu_4$-THF SOLUTIONS

| Molarity $eq\ l^{-1}$ | $\Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| 0.05216 | 19.62 | 0.8847 | 5.20 |
| 0.09525 | 21.08 | 0.8843 | 5.85 |
| 0.1145 | 21.03 | 0.8845 | 5.74 |
| 0.1674 | 21.20 | 0.8817 | 6.52 |
| 0.2027 | 18.90 | 0.8880 | 6.68 |
| 0.2094 | 20.26 | 0.8877 | 6.70 |
| 0.2881 | 19.46 | 0.8895 | 7.56 |
| 0.3348 | 17.91 | 0.8880 | 12.8 |
| 0.4687 | 15.57 | 0.8941 | 10.7 |

another. This shearing is resisted by intermolecular attractions in electrolyte solutions which are of two types: (1) short range solvent-solvent, ion-solvent, and solute-solute forces; and (2) long range Coulombic forces between ions.

The decrease in viscosity occurring up to approximately the 1:1 THF to NaAl(n-butyl)$_4$ mole ratio can be attributed to the break-up of the ion aggregates as a result of the formation of the stable 1:1 complex. After the 1:1 complex forms, the viscosity remains relatively constant at low mole ratio values. Since cyclohexane is a non-interacting solvent, ion solvent interactions between cyclohexane and NaAl(n-butyl)$_4$ and its ions do not exist and do not contribute to this shearing force. At mole ratios between 1:1 and 4:1 the important contributions to the viscosity will be due to long range Coulombic forces between the ions. These should remain relatively constant until the 4:1 complex has formed. Only upon the addition of large amounts of THF will the viscosity again begin to change due to a decrease in these long range forces caused by a further shielding of the $Na^+$ ion by additional layers of THF molecules. This trend is exhibited in the study made for the complete range of mole ratios from pure cyclohexane to pure THF for 0.2094 M NaAl(n-butyl)$_4$ solutions.

The formation of two immiscible liquid phases at ratios between 10:1 and 15:1 can not be explained. Hogen-Esch and Smid[14] observed a similar phenomenon with fluorenylsodium solutions in THF

upon the addition of dimethylsulfoxide (DMSO). A precipitate formed which they attributed to a polymeric aggregate which breaks up and dissolves upon the addition of excess DMSO. The composition of the two phases in the NaAl(n-butyl)$_4$-THF-cyclohexane system was not determined. Nuclear magnetic resonance studies would probably show, as they do for the two phases formed in the NaAl(n-butyl)$_4$-DME-cyclohexane system, the existence of salt, THF, and cyclohexane in both phases with most of the salt extracted to the denser phase at the higher mole ratio values.

## D. Ion-solvent Interaction: $Na^+$-DME

Equivalent conductances for solutions of 0.05177 M, 0.1031 M, and 0.2017 M NaAl(n-butyl)$_4$ in solutions of cyclohexane with small amounts of DME added are presented as a function of the mole ratio of DME to NaAl(n-butyl)$_4$ in Figures 6 and 7. Equivalent conductance, density, and viscosity values for these solutions are contained in Table 4.

### 1. Conductance

The general shape of these conductance curves follows the pattern established for those obtained in the THF studies. A rapid rise in equivalent conductance occurs upon the addition of DME, followed by a decrease, a possible rise, formation of two immiscible liquid phases, and a rise to conductance values for DME solutions comparable in magnitude to those of the pure THF solutions. With

TABLE 4

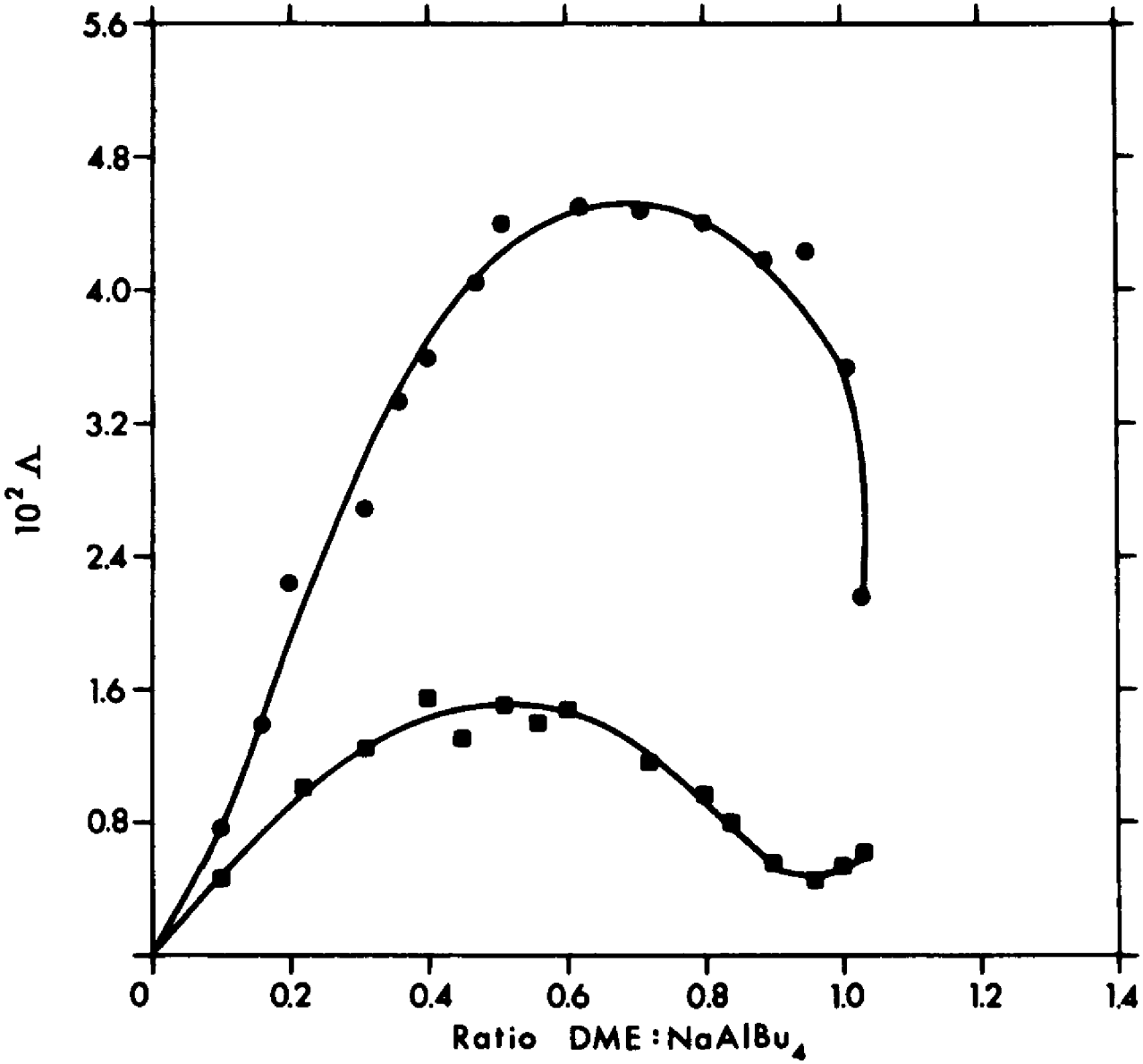
EFFECT OF DME ON THE EQUIVALENT CONDUCTANCES, DENSITIES, AND VISCOSITIES OF $NaAlBu_4$-CYCLOHEXANE SOLUTIONS

| Ratio DME:$NaAlBu_4$ | $10^2 \Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| | 0.05177 M $NaAlBu_4$ | | |
| 0.10 | 0.4692 | 0.7754 | 12.5 |
| 0.22 | 1.009 | 0.7752 | 10.9 |
| 0.31 | 1.247 | 0.7739 | 10.5 |
| 0.40 | 1.551 | 0.7740 | 9.94 |
| 0.45 | 1.304 | 0.7748 | 9.98 |
| 0.51 | 1.510 | 0.7724 | 9.40 |
| 0.56 | 1.405 | 0.7742 | 9.71 |
| 0.60 | 1.480 | 0.7760 | 9.54 |
| 0.72 | 1.163 | 0.7757 | 9.48 |
| 0.80 | 0.9691 | 0.7738 | 9.35 |
| 0.84 | 0.5843 | | |
| 0.90 | 0.5600 | 0.7744 | 9.36 |
| 0.96 | 0.4559 | 0.7776 | 9.42 |
| 1.00 | 0.5436 | 0.7749 | 9.42 |
| 1.03 | 0.6220 | 0.7750 | 9.35 |
| 1.24 | Two Phases | | |
| | 0.1031 M $NaAlBu_4$ | | |
| 0.00 | 0.4605 | 0.7747 | 22.7 |
| 0.10 | 0.7632 | 0.7760 | 16.2 |
| 0.16 | 1.392 | 0.7779 | 14.1 |
| 0.20 | 2.234 | 0.7767 | 12.6 |
| 0.31 | 2.682 | 0.7762 | 12.3 |
| 0.36 | 3.335 | 0.7774 | 11.9 |
| 0.40 | 3.585 | 0.7779 | 11.7 |
| 0.47 | 4.048 | 0.7766 | 11.4 |
| 0.51 | 4.398 | 0.7755 | 11.3 |
| 0.62 | 4.507 | 0.7768 | 10.8 |
| 0.71 | 4.485 | 0.7775 | 10.8 |
| 0.80 | 4.412 | 0.7776 | 10.4 |
| 0.89 | 4.187 | 0.7773 | 10.4 |
| 0.95 | 4.233 | 0.7783 | 10.2 |
| 1.01 | 3.534 | 0.7797 | 10.4 |
| 1.10 | Two Phases | | |
| | 0.2017 M $NaAlBu_4$ | | |
| 0.00 | 0.04624 | 0.7788 | 37.1 |
| 0.07 | 0.7312 | 0.7784 | 24.6 |

| Ratio DME:$NaAlBu_4$ | $10^2 \Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| | 0.2017 M $NaAlBu_4$ (Cont.) | | |
| 0.10 | 1.047 | 0.7773 | 24.0 |
| 0.18 | 2.173 | 0.7792 | 19.6 |
| 0.30 | 4.138 | 0.7811 | 17.5 |
| 0.31 | 4.423 | 0.7822 | 17.0 |
| 0.41 | 6.763 | 0.7793 | 15.2 |
| 0.46 | 7.797 | 0.7793 | 14.9 |
| 0.50 | 8.709 | 0.7805 | 14.2 |
| 0.56 | 9.989 | 0.7801 | 13.8 |
| 0.61 | 10.43 | 0.7793 | 13.8 |
| 0.66 | 11.35 | 0.7806 | |
| 0.71 | 11.73 | 0.7805 | 13.9 |
| 0.75 | 12.33 | 0.7817 | |
| 0.80 | 15.67 | 0.7823 | 13.9 |
| 0.94 | Two Phases | | |

FIGURE 6

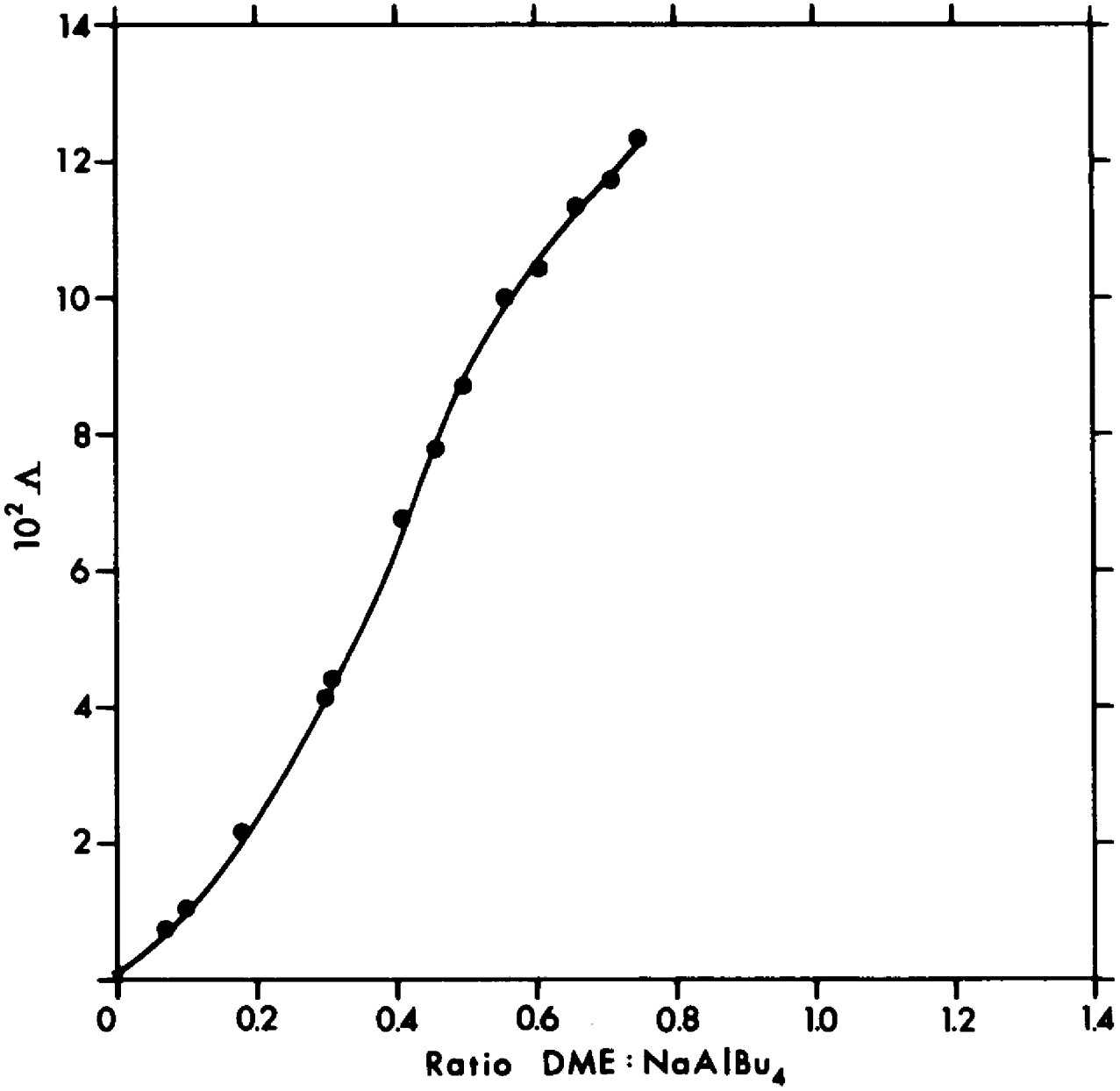
EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE-DME MIXTURES AS A FUNCTION OF THE MOLE RATIO DME:$NaAlBu_4$




Concentration $NaAlBu_4$: ■ - 0.05177 M, ● - 0.1031 M

FIGURE 7

EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE-DME MIXTURES AS A FUNCTION OF THE MOLE RATIO DME:$NaAlBu_4$




Concentration $NaAlBu_4$ = 0.2017 M

increasing salt concentration, the drop in conductance following the initial peak value tends to disappear until at some concentration between 0.1031 M and 0.2017 M only one inflection point occurs.

Significant differences are to be noted between the THF and DME systems which may be due to the greater solvating power of DME. The initial peak conductance at concentrations of 0.05177 M and 0.1031 M salt occurs at a mole ratio of about 0.5:1 instead of 1:1 implying only one-half of the $Na^+$ ions are involved as conducting species. This implication may indicate an equilibrium involving the formation of a triple ion such as:

$$[NaAl(\underline{n}\text{-butyl})_4]_2 = Na^+ + Na[Al(\underline{n}\text{-butyl})_4]_2^-$$

This dissociation of the ion aggregate, as was pointed out for the case of THF, may be promoted by direct reaction between the ion aggregate and DME or by complexation of the free $Na^+$ ion with DME.

With DME an equilibrium involving both the monodentate complexed $Na^+$ ion and the bidentate complexed ion may occur:

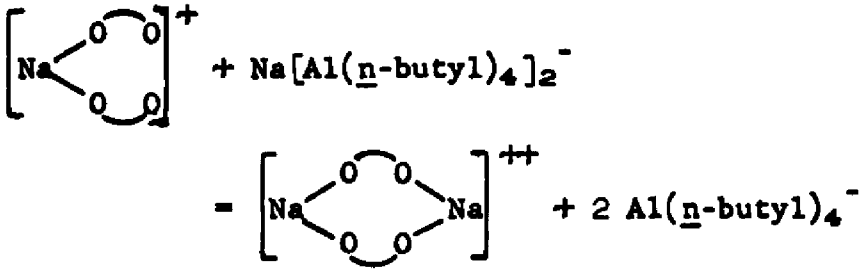
$$[Na\text{-}O\frown O]^+ = \left[Na\begin{smallmatrix}O\\O\end{smallmatrix}\right]^+$$

After the 0.5:1 mole ratio a second molecule of DME might add to these complex ions. A two-coordinated ion may then exist in equilibrium with a four-coordinated ion.

$$[O\frown O\text{-}Na\text{-}O\frown O]^+ = \left[\begin{smallmatrix}O\\O\end{smallmatrix}Na\begin{smallmatrix}O\\O\end{smallmatrix}\right]^+$$

Both types of ions would be expected, as a result of decreased

mobility, to decrease the equivalent conductance. Formation of bridged species from the reaction of the monodentate $Na(DME)_2^+$ ion with a $Na[Al(\underline{n}\text{-butyl})_4]_2^-$ triple ion could also occur.



The bridged ion, $[Na_2(DME)_2]^{++}$, could form ion aggregates so stable that another molecule of DME would not add until the characteristics of the solvent system are significantly changed by the addition of a large excess of DME. This new species because of a greater ion size, decreased mobility, and greater tendency to form ion aggregates would, compared with $[Na(DME)_2]^+$ contribute to a further decrease in conductance and might be responsible for the formation of two immiscible liquid phases. These studies do not offer significant proof for the proposed mechanism. Trigg's suggestion of the existence of a triple ion of the type -+- may be indicated.[34]

Comparison of Figures 6 and 7 show that a significant difference in the ionic species present in solution exists between the 0.5:1 and 0.8:1 mole ratios at high salt concentrations. For THF the change in shape in the conductance curve at these higher concentrations was ascribed to that of a different conductance mechanism. The inflection point in Figure 7 may indicate the same occurrance for the DME system.

An alternative explanation is that a two-phase system might begin to form after the 0.5:1 mole ratio and not be detected visually. The appearance of two phases in these solutions is easily detected by the appearance of two types of DME in the NMR spectrum. Since conductance measurements were determined at 25° C and NMR spectra were obtained at 36° C, it is possible that an immiscible system at 25° C might be miscible at the higher temperature. This, however, is unlikely in the light of the conductance curve for the 0.2017 M solution of $NaAl(\underline{n}\text{-butyl})_4$. At this higher concentration, the formation of two phases would be expected to be more likely than in the other instances. Yet the conductance is observed to continue to increase after the 0.5:1 ratio of DME to $NaAl(\underline{n}\text{-butyl})_4$. Nevertheless, additional NMR studies of this system need to be made at lower temperatures to eliminate this possibility. At 32° C two phases were not observed in 0.2017 M $NaAl(\underline{n}\text{-butyl})_4$ solutions containing ratios of DME to salt greater than 0.85 and less than 1.10. At 25° C two immiscible liquid phases were clearly visible.

At salt concentrations of 0.05177 M and 0.1031 M, two liquid phases begin to form past the 1:1 mole ratio value. Homogeneity can be achieved for low mole ratio solutions by raising the temperature of the solution. Prolonged heating at 70° C of a solution containing DME and salt at a 10:1 mole ratio does not yield a homogeneous solution. Two phases occur up to a 10:1 mole ratio in 0.1031 M solutions. This ratio was the highest which was prepared.

Again, if the possibility of an unobserved two-phase system is considered, the rise in the equivalent conductance of the 0.1031 M conductance curve at 1:1 may not be real. Analogy with the study made for 0.2094 M $NaAl(\underline{n}\text{-butyl})_4$ solutions in THF-cyclohexane as well as the measurements in DME solutions presented in Table 5 indicate that miscibility will be achieved at higher mole ratios and the equivalent conductance will again rise rapidly. With the 0.2017 M salt system, two phases occur at lower DME:salt ratios than with those at lower concentrations.

Nuclear magnetic resonance data indicate the existence of $NaAl(\underline{n}\text{-butyl})_4$, DME, and cyclohexane in both phases of the two-phase systems. In the denser phase, the concentration of both the DME and the $NaAl(\underline{n}\text{-butyl})_4$ are greater than in the cyclohexane phase.

2. Viscosity

Viscosity trends are similar to those for the THF solutions. A rapid decrease in viscosity occurs before the 0.5:1 mole ratio of solvent to salt followed by a leveling off to a constant value. These trends can be explained in the same way as those for the THF solutions. Up to 0.5:1 ratios the viscosity will decrease due to a dissociation of the ion aggregate caused by the formation of a stable complex. At mole ratios past this value, the long range Coulombic forces between ions, being the most important factor contributing to the viscosity, remain relatively constant until the formation of two immiscible solutions at about 1:1 mole ratios.

TABLE 5

EFFECT OF CONCENTRATION ON THE EQUIVALENT CONDUCTANCES, DENSITIES, AND VISCOSITIES OF $NaAlBu_4$-DME SOLUTIONS

| Molarity<br>eq $l^{-1}$ | $\Lambda$<br>$cm^2\ ohm^{-1}\ eq^{-1}$ | Density<br>g/ml | Viscosity<br>millipoise |
|---|---|---|---|
| 0.05202 | 18.17 | 0.8633 | 4.57 |
| 0.1035 | 21.58 | 0.8634 | 4.90 |
| 0.2018 | 23.99 | 0.8657 | 6.59 |

3. Comparison of Ion-solvent Interaction: $Na^+$-DME and $Na^+$-THF

Similarities in physical properties (density, dielectric constant, viscosity, etc.) between DME and THF would tend to support the belief that similar equilibria and mechanisms occur in each system with differences attributed to the different solvating power of the two ethers.

Studies with aryl anions, i.e., fluorenyl and dibutylnaphthalate, show that the solvation of the $Na^+$ ion by THF results in a temperature dependent equilibrium between solvent separated ion pairs and contact ion pairs.[14,17,23,28] Only solvent separated ion pairs are formed with DME. At 25° C the equilibrium in the $Na^+$-THF system is to the side of the contact ion pair. For fluorenylsodium at these conditions, the fraction of solvent separated ion pairs is 0.05.[14] The relative distribution between solvent separated ion pairs and contact ion pairs primarily depends on the basicity of the coordinating agent, but it also must depend to some extent on the basicity of the anion. These results might again be applied to the behavior of ion aggregates in the salt concentration range of 0.05-0.20 M. The major portion of the research reported in this Dissertation was made at these concentrations.

Even though the type of aggregate of $NaAl(n\text{-butyl})_4$ existing in cyclohexane is unknown, conductance studies of solutions of this salt in cyclohexane show the formation of stable complexes between THF and the $Na^+$ ion and DME and the $Na^+$ ion. In both

instances the conductance of the solution at this point is significantly greater than that of the cyclohexane-salt solution. The original ion aggregate appears to have dissociated into a less complex ionic conducting species. Thus, it may be concluded that solvent separated ion pairs may exist as a principal species in solutions of $NaAl(\underline{n}\text{-butyl})_4$ in cyclohexane-THF solvent systems since the $Al(\underline{n}\text{-butyl})_4^-$ ion is expected to be less basic than the aryl anions which were previously mentioned. As a result of this difference in base strength, a solvent separated ion pair containing the $Al(\underline{n}\text{-butyl})_4^-$ ion should generally dissociate to a greater extent and be more reactive than a solvent separated ion pair containing an aryl anion.

Since the stable complex formed between DME and the $Na^+$ ion occurs at a mole ratio of 0.5:1, the prediction of a major species present in solution at this point is subject to speculation. Hogen-Esch and Smid established the fact that a complexation between contact ion pairs and THF and DME can occur.[17] A similar type of reaction between the coordinating solvent and the ion aggregate might occur. Dissociation of the solvated ion aggregate could produce a $NaDME^+$ ion and a triple ion. However, the higher concentration of salt used in this system and the use of a non-interacting solvent of low dielectric constant should lead to a cautious application of the conclusions determined for ion pairs to our systems. The theories of Fuoss and Kraus[45] and the recent work of Trigg[34] would indicate that triple ions can possibly be present at the concentrations used in these studies.

For the less concentrated NaAl(n-butyl)$_4$ solutions in cyclohexane at 0.05177 M and 0.1031 M, the viscosities following the peak conductance value are about the same for both the THF and DME solutions. This may indicate the presence of similar types of particles in both systems. If the proposal is true, then the major species existing at the 0.5:1 mole ratio may be $NaDME^+$ and a triple anion. Studies designed to investigate the existence of the triple ion in these solutions as well as in the THF solutions would be helpful in describing the interaction of the electrolyte with the solvent in these systems.

For 0.05 M NaAl(n-butyl)$_4$ solutions, the peak conductance in DME-cyclohexane solutions (DME:salt = 0.5:1) is approximately three times that of the subsequent minimum value, while this factor for THF (THF:salt = 1:1) is about 15. Conductance values for comparable ratios and salt concentrations with DME are about three times those for similar THF solutions.

Two immiscible liquid phases begin to occur with the $Na^+$ ion-DME systems at lower solvent:salt mole ratios than with the $Na^+$ ion-THF systems. The appearance of a single inflection point in the conductance curve also occurs at a lower salt concentration with DME added as a coordinating solvent. These results can be attributed to the greater solvating power of DME as compared with THF.

## E. Complexation with Weak Bases

Studies of the complexation of the $Na^+$ ion with weak bases in solvents of low dielectric constant have not been practical because of the low solubility of suitable sodium salts in these solvents. In systems where significant solubility occurs, the basic nature of the solvent complicates the problem by itself interacting with the $Na^+$ ion. Thus the solubility of $NaAl(\underline{n}\text{-butyl})_4$ in cyclohexane, a non-interacting solvent, provides a unique system for studies of this type.

### 1. Benzene

Table 6 and Figure 8 present data for $NaAl(\underline{n}\text{-butyl})_4$-benzene-cyclohexane solutions. The conductance is seen to increase with increasing mole ratio of benzene to salt with no inflection points observed at any of the salt concentrations studied. Viscosity changes are small with increasing amounts of benzene added in contrast to the rapid changes observed for THF and DME. Nuclear magnetic resonance spectra show no interaction between cyclohexane and benzene.[37] In addition, no significant chemical shift in the protons of benzene in cyclohexane-$NaAl(\underline{n}\text{-butyl})_4$ solutions are observed in the concentration range which was studied. Therefore, it can be concluded that no specific interaction between the $Na^+$ ion and benzene molecules occurs.

At higher mole ratios of benzene to salt, a two-phase system consisting of white needle-like crystals and a clear solution

TABLE 6

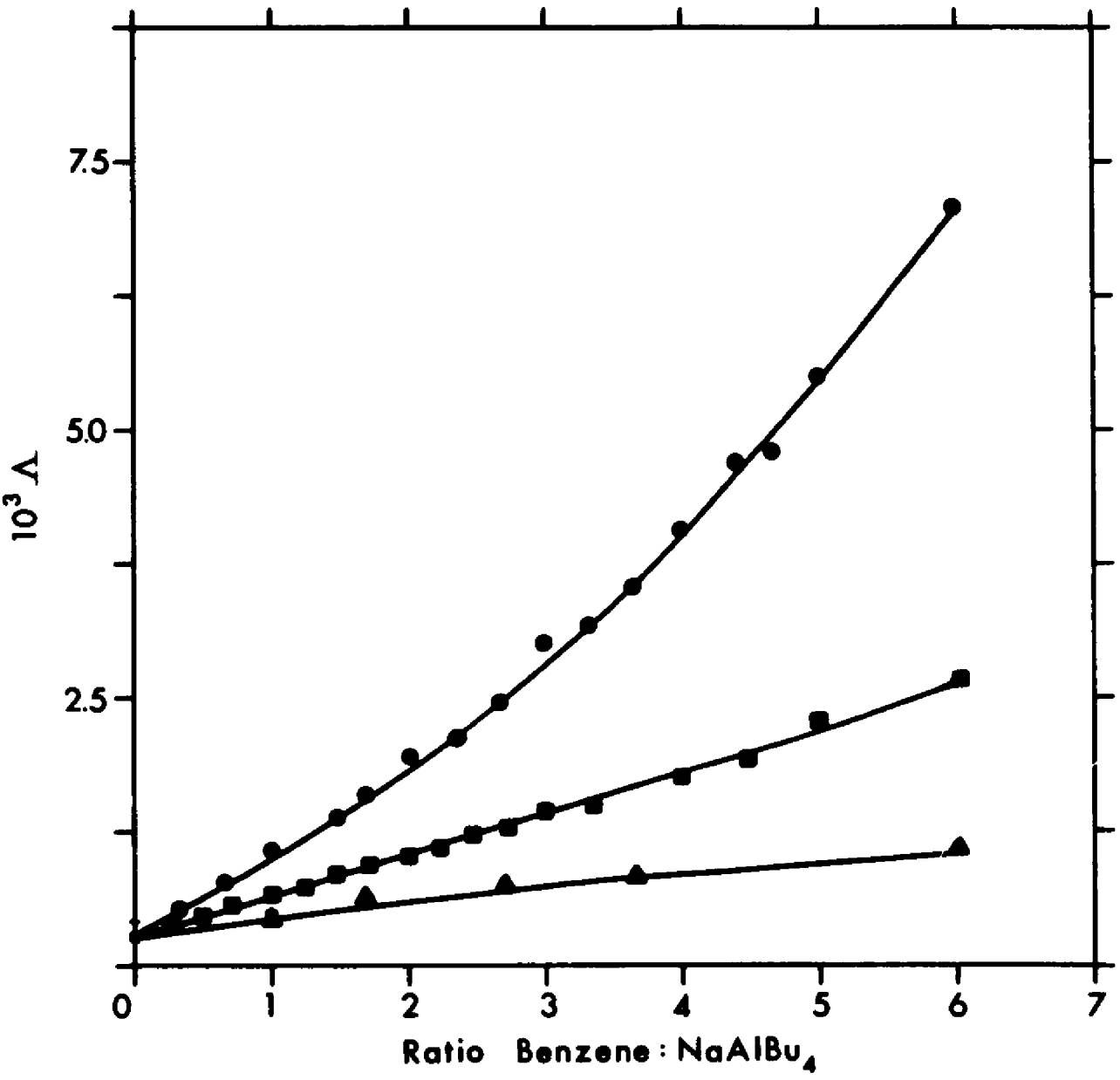
EFFECT OF BENZENE ON THE EQUIVALENT CONDUCTANCES, DENSITIES, AND VISCOSITIES OF $NaAlBu_4$-CYCLOHEXANE SOLUTIONS

| Ratio Benzene:$NaAlBu_4$ | $10^3 \Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| | 0.04776 M $NaAlBu_4$ | | |
| 0.00 | 0.4146 | 0.7740 | 14.1 |
| 0.71 | 0.5883 | 0.7741 | 15.0 |
| 1.00 | 0.5028 | 0.7752 | 15.5 |
| 1.70 | 0.6488 | 0.7759 | 14.5 |
| 2.71 | 0.7504 | 0.7760 | 14.2 |
| 3.67 | 0.8498 | 0.7747 | 12.8 |
| 6.02 | 1.100 | 0.7770 | 12.1 |
| | 0.1032 M $NaAlBu_4$ | | |
| 0.00 | 0.2798 | 0.7759 | 23.8 |
| 0.27 | 0.3714 | | |
| 0.51 | 0.4674 | 0.7759 | 23.3 |
| 0.73 | 0.5624 | 0.7766 | 22.9 |
| 1.01 | 0.6722 | 0.7759 | 20.6 |
| 1.26 | 0.7255 | 0.7749 | 23.9 |
| 1.48 | 0.8380 | 0.7761 | 22.6 |
| 1.73 | 0.9434 | 0.7762 | 21.6 |
| 2.01 | 1.023 | 0.7777 | 21.9 |
| 2.25 | 1.114 | 0.7760 | 22.8 |
| 2.48 | 1.225 | 0.7773 | 22.3 |
| 2.75 | 1.279 | 0.7773 | 21.7 |
| 3.01 | 1.442 | | |
| 3.36 | 1.497 | 0.7774 | 21.6 |
| 4.01 | 1.758 | 0.7769 | 20.8 |
| 4.49 | 1.923 | 0.7796 | 20.1 |
| 5.01 | 2.284 | 0.7779 | 19.5 |
| 6.03 | 2.660 | 0.7803 | 19.0 |
| | 0.2023 M $NaAlBu_4$ | | |
| 0.00 | 0.2654 | 0.7786 | 36.2 |
| 0.34 | 0.5215 | 0.7778 | 36.4 |
| 0.67 | 0.7718 | 0.7784 | 35.6 |
| 1.01 | 1.082 | 0.7797 | 34.5 |
| 1.50 | 1.383 | 0.7797 | 32.2 |
| 1.70 | 1.598 | 0.7815 | 33.4 |
| 2.02 | 1.960 | 0.7817 | 31.5 |
| 2.36 | 2.131 | 0.7814 | 29.7 |

| Ratio Benzene:$NaAlBu_4$ | $10^3$ Λ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| | 0.2023 M $NaAlBu_4$ (Cont.) | | |
| 2.68 | 2.462 | 0.7825 | 30.4 |
| 3.00 | 3.005 | | |
| 3.33 | 3.173 | 0.7829 | 28.9 |
| 3.65 | 3.535 | 0.7829 | 26.9 |
| 4.00 | 4.066 | 0.7840 | 27.5 |
| 4.40 | 4.704 | 0.7848 | 26.8 |
| 4.67 | 4.799 | 0.7866 | 25.5 |
| 5.00 | 5.490 | 0.7872 | 25.1 |
| 6.00 | 7.076 | 0.7891 | 23.7 |
| 8.04 | 11.12 | 0.7904 | 20.1 |
| 10.17 | Two Phases | | |

FIGURE 8

EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE-BENZENE MIXTURES AS A FUNCTION OF THE MOLE RATIO BENZENE:$NaAlBu_4$




Concentration $NaAlBu_4$: ▲ - 0.04776 M, ■ - 0.1032 M, ● - 0.2023 M

begins to form slowly at temperatures between 25° C and 33° C. A day after preparation of this solution, the yield of white crystals has increased noticeably. This precipitate can be filtered in the nitrogen dry box, dried under a nitrogen atmosphere, and is apparently unreactive with small amounts of oxygen or moisture. It is readily soluble in THF and insoluble in benzene at temperatures up to 60° C. Solubility does not appear to increase with temperature. Benzene can react with $NaAlEt_4$ in the presence of sodium alkoxides to form sodium tetraphenylaluminate at elevated temperatures.[47,48]

$$NaAlEt_4 + 4\ C_6H_6 \xrightarrow{NaOR} NaAlPh_4 + 4\ C_2H_6$$

This reaction might occur with $NaAl(\underline{n}\text{-butyl})_4$. Investigation of this possibility should be pursued.

2. Toluene

Analogous studies with toluene were also made, and conductance and NMR measurements indicate no interaction with the $Na^+$ ion at a salt concentration of 0.1994 M in cyclohexane. The results of this study are presented in Table 7 and Figure 9. Similar types of behavior are expected to be exhibited by benzene and toluene.

Measurements were made within a 36-hour period with care taken to insure that the nitrogen dry box was free from traces of moisture, oxygen, and ether vapors. A sample of freshly prepared salt was used to be certain of the absence of trace amounts of alkoxides. These precautions were taken to decrease the possibility

TABLE 7

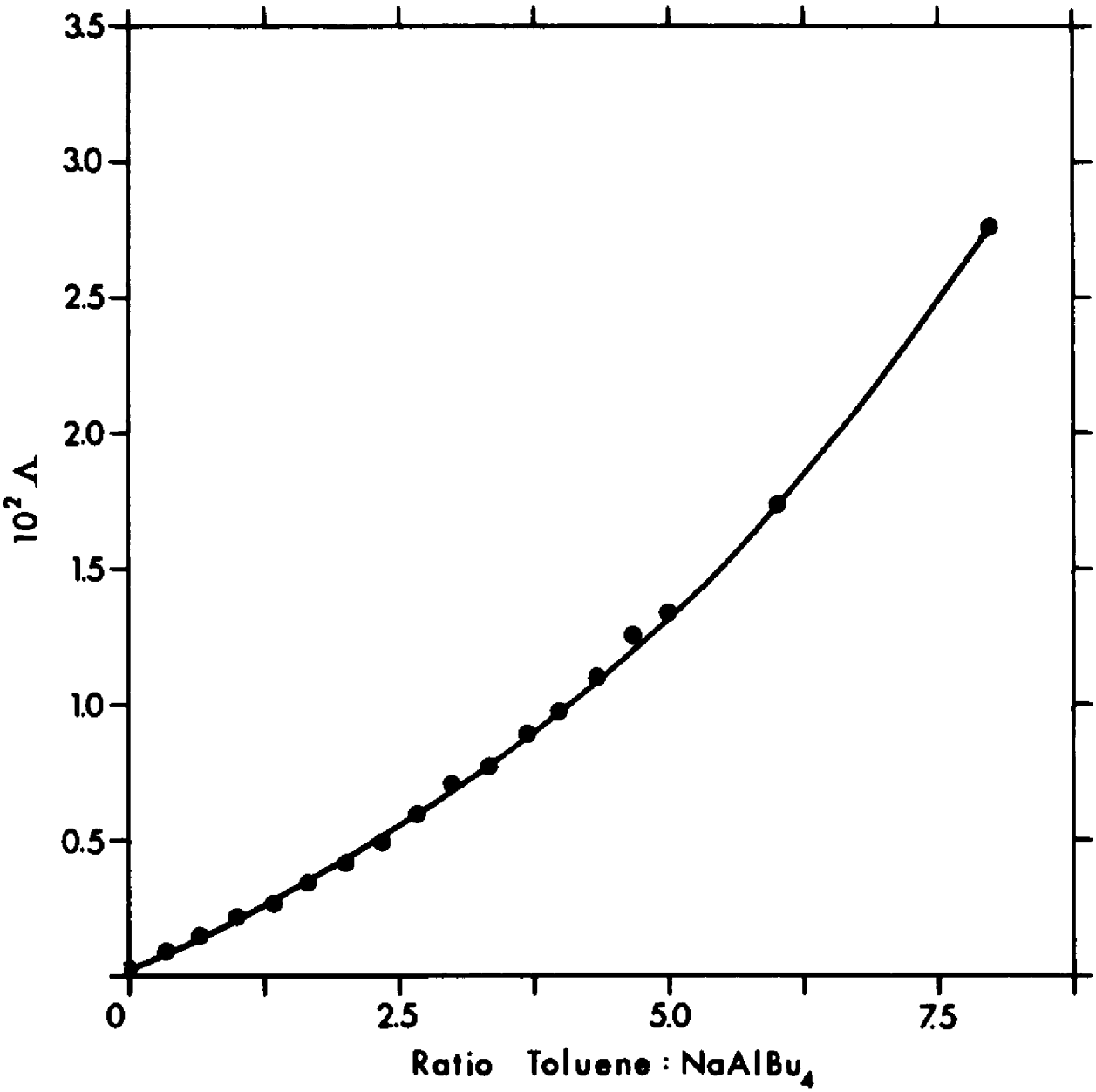
EFFECT OF TOLUENE ON THE EQUIVALENT CONDUCTANCES, DENSITIES, AND VISCOSITIES OF $NaAlBu_4$-CYCLOHEXANE SOLUTIONS

| Ratio Toluene:$NaAlBu_4$ | $10^2 \Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ | Density g/ml | Viscosity millipoise |
|---|---|---|---|
| | 0.1994 M $NaAlBu_4$ | | |
| 0.00 | 0.03530 | 0.7809 | 43.5 |
| 0.34 | 0.09386 | 0.7791 | 39.3 |
| 0.67 | 0.1493 | 0.7800 | 36.6 |
| 1.00 | 0.2177 | 0.7818 | |
| 1.34 | 0.2676 | 0.7812 | 34.2 |
| 1.67 | 0.3488 | 0.7818 | 33.1 |
| 2.01 | 0.4168 | 0.7817 | 32.3 |
| 2.34 | 0.5002 | 0.7836 | 30.2 |
| 2.67 | 0.5955 | 0.7839 | 28.9 |
| 3.00 | 0.7098 | 0.7839 | |
| 3.34 | 0.7789 | 0.7845 | 27.2 |
| 3.70 | 0.8923 | 0.7844 | 26.2 |
| 4.00 | 0.9769 | 0.7868 | 24.9 |
| 4.34 | 1.103 | 0.7863 | 23.8 |
| 4.67 | 1.260 | 0.7877 | 22.8 |
| 5.00 | 1.337 | 0.7863 | 22.6 |
| 6.01 | 1.740 | 0.7893 | 20.8 |
| 8.00 | 2.763 | 0.7921 | 17.8 |
| 10.00 | 3.962 | 0.7959 | 15.2 |
| 43.83* | 12.61 | 0.8611 | 6.79 |

*Pure Toluene Solution

FIGURE 9

EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE-TOLUENE MIXTURES AS A FUNCTION OF THE MOLE RATIO TOLUENE:$NaAlBu_4$




Concentration $NaAlBu_4$ = 0.1994 M

of substitution of butyl groups in the Al(n-butyl)$_4^-$ ion by tolyl groups. Solid particles were not observed in the toluene solutions upon storage for several days in sealed volumetric flasks. Toluene, as expected, is less reactive than benzene in the replacement of the alkyl groups in the Al(n-butyl)$_4^-$ ion.

The steeper slope of the conductance curve for the toluene solutions as compared with the slope for the benzene solutions at a similar salt concentration results from a greater change in viscosity over the mole ratio range studied.

3. Triethylamine

Nuclear magnetic resonance studies by Schaschel and Day[21] have shown that triethylamine forms a much weaker complex with the $Na^+$ ion than does THF in solutions of NaAl(n-butyl)$_4$ in cyclohexane. The conductance study presented in Table 8 and Figure 10 supports this conclusion. While this study was not extensive, it shows that only a very weak complex of triethylamine with the $Na^+$ ion is formed since measurements extending to the pure triethylamine solution show little change in equivalent conductance.

F. Dielectric Constant and Ion-solvent Interaction

The conductance curves of the NaAl(n-butyl)$_4$-THF-cyclohexane system (Figure 2) for the low salt concentrations can be interpreted in a manner indicating the possibility of distinguishing between a specific ion-solvent effect and a solvent dielectric constant effect.

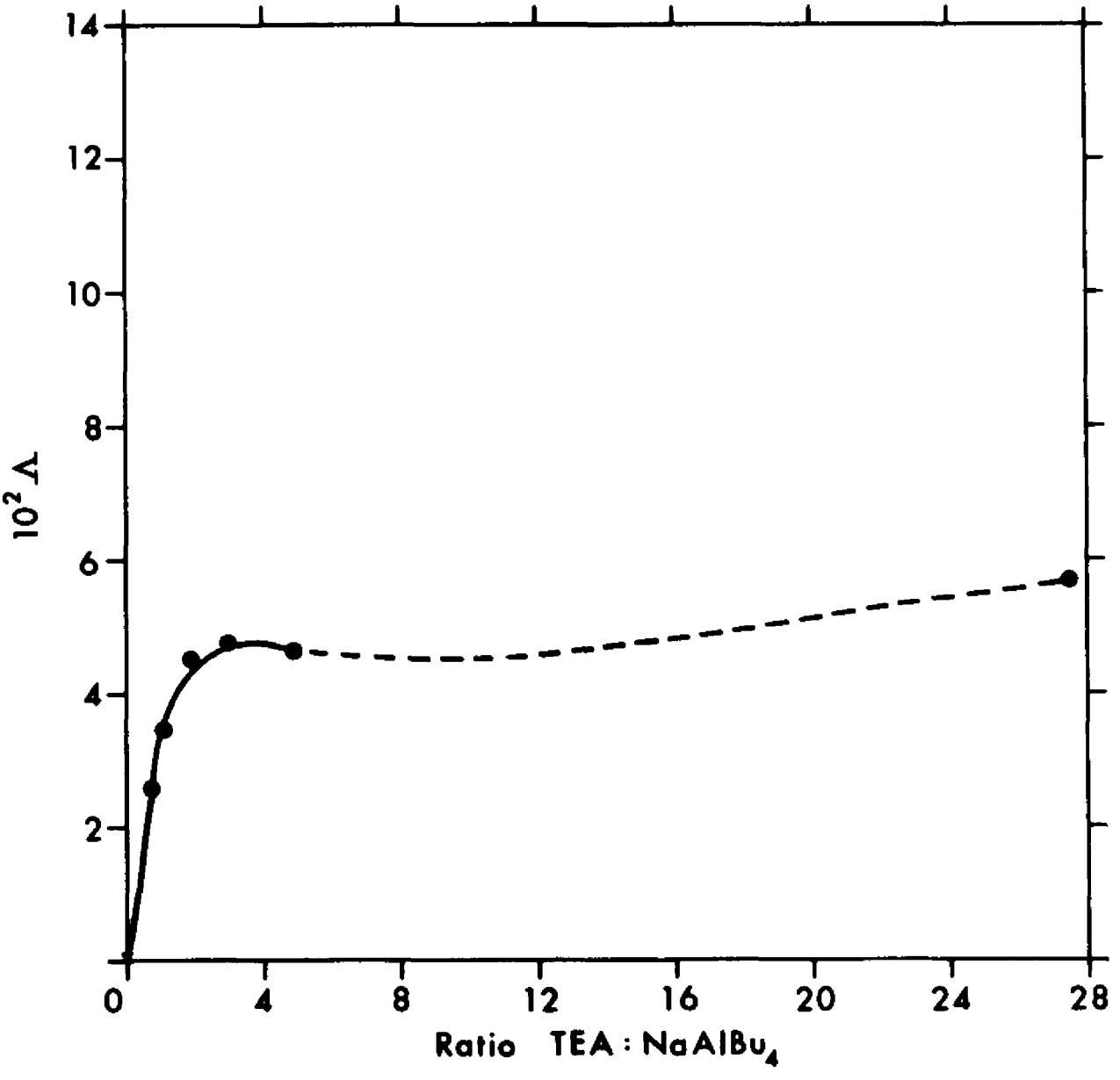
TABLE 8

EFFECT OF TRIETHYLAMINE ON THE EQUIVALENT CONDUCTANCES OF $NaAlBu_4$-CYCLOHEXANE SOLUTIONS

| Ratio TEA:$NaAlBu_4$ | $10^2 \Lambda$ $cm^2\ ohm^{-1}\ eq^{-1}$ |
|---|---|
| --------0.2684 M $NaAlBu_4$-------- | |
| 0.73 | 2.576 |
| 1.11 | 3.470 |
| 1.91 | 4.501 |
| 3.00 | 4.752 |
| 4.95 | 4.632 |

FIGURE 10

EQUIVALENT CONDUCTANCE OF $NaAlBu_4$ IN CYCLOHEXANE-TRIETHYLAMINE MIXTURES AS A FUNCTION OF THE MOLE RATIO TEA:$NaAlBu_4$




Concentration $NaAlBu_4$ = 0.2684 M

At 25° C the dielectric constant of THF is 7.39 and that of cyclohexane is 2.01. Addition of THF is expected to increase the solvent dielectric constant. However, the stability of the 1:1 complex leads to the assumption that no free THF exists up to a 1:1 ratio. The increase in equivalent conductance up to this point can not be attributed to an increase in the solvent dielectric constant. It appears to result from the formation of the stable 1:1 complex between the $Na^+$ ion and THF.

Qualitatively ion-solvent interaction may be interpreted in terms of an ion size effect. The stability of the ion aggregate will decrease with an increase in the effective cation size. This results in an increase in the number of charge carriers. Further complexation, however, leads to a decrease in cation mobility. The conductance behavior prior to the 4:1 mole ratio can then be considered in terms of ion size rather than the solvent dielectric constant since the amounts of free THF expected to be present will insignificantly affect the bulk dielectric constant of the solvent. The increase in equivalent conductance at approximately the 4:1 mole ratio may be attributed to an increase in the solvent dielectric constant. In this region the separation of the effects of ion size and dielectric constant is not possible without a similar study as a function of cation size using sufficiently large cations so that ion-solvent interaction can be neglected.

TABLE 9

PHYSICAL PROPERTIES OF SOLVENTS AT 25° C

| Solvent | Density g/ml | | Viscosity millipoise | | Dielectric Constant |
|---|---|---|---|---|---|
| | Expt. | Lit. | Expt. | Lit. | |
| Benzene | 0.8720 | 0.8736 | 6.06 | 6.03 | 2.27 |
| Cyclohexane | 0.7725 | 0.7739 | 9.08 | 9.00 | 2.01 |
| DMK | 0.8594 | 0.8621 | 4.36 | 4.32 | 6.80 |
| THF | 0.8806 | 0.8829 | 4.77 | 4.53 | 7.39 |
| Toluene | 0.8604 | 0.8623 | 5.63 | 5.58 | 2.38 |
| Triethylamine | | 0.7235 | | 3.41 | 3.08 |

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## VITA

Cecil N. Hammonds, Jr., was born in Omaha, Nebraska on September 6, 1935. Attending parochial elementary schools in Los Angeles, California, Salt Lake City, Utah, Louisville, Kentucky, and Kansas City, Missouri, he was graduated from De La Salle Military Academy, Kansas City, Missouri in 1952. Upon receiving a Bachelor of Science degree in chemistry from the University of Missouri at Kansas City in June 1956, he entered the University of Kansas where a Master of Science degree in Analytical Chemistry was awarded in October 1959.

Since September 1959, he has been a member of the chemistry faculty of the Metropolitan Junior College - Kansas City, where he is presently serving as Chairman of the Chemistry Department.

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**EXAMINATION AND THESIS REPORT**

**Candidate:** Cecil Noah Hammonds Jr.

**Major Field:** Chemistry

**Title of Thesis:** A Conductance Study of Ion-Solvent Interaction

**Approved:**

Major Professor and Chairman

Dean of the Graduate School

**EXAMINING COMMITTEE:**

**Date of Examination:**

September 23, 1968